# ASPECTS OF THE CHEMISTRY OF

# 1,2,5-OXAZAPHOSPH(V)OLES

by

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Finally, thanks are due to the University of Edinburgh for the award of a Scholarship during the period of this work.

## Declaration

I declare that this thesis is my own composition, that the work of which it is a record was carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh under the supervision of Professor J. I. G. Cadogan since 1st October 1976, the date of my admission as a research student.

The following courses have been attended: Organic Chemistry Seminars, Edinburgh University Chemistry Department (3 years attendance); Organic Sulphur Compounds in General Synthesis (5 lectures), Dr. D. Leaver; High Pressure Liquid Chromatography (5 lectures), staff of Wolfson Liquid Chromatography Unit; Exploitation of Inventiveness in the Oil Industry (5 lectures), staff of BP Oil Ltd.; Strategy of Organic Synthesis (5 lectures), Dr. I. Gosney; Chemistry at its most Colourful (5 lectures), staff of ICI Organics; Stereochemistry - Basic and Advanced (5 lectures), Dr. H. McNab; The Bio-organic Chemistry of Drugs, Toxins and other Xenobiotics (5 lectures), Dr. A. G. Rowley.

## Abstract

High temperature deoxygenation of 2-aryl-1-phenylnitroethenes with triethyl phosphite gave products considered to arise from the vinyl nitrene. Comparison of the products with those obtained by deoxygenation of the corresponding 3,4-diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(v)oles showed that these phosph(v)oles were likely intermediates in the nitro deoxygenation reaction. In two cases, the corresponding 1,2,5-oxazaphosph(v)oles lacking the N-oxide function were isolated as stable solids. This suggested the possibility of an alternative deoxygenation mechanism operative in the case of nitroethenes. Thermolysis of the 1,2,5-oxazaphosph(v)oles provided good evidence for the intermediacy of the vin yl nitrene. Convincing evidence for the involvement of the nitrosoethene could not be obtained, and all attempts to synthesise 1,2-diphenyl-1-nitrosoethene met with failure. A mechanism involving the two oxazaphosph(v)oles was shown to be feasible, however, although it did not appear to be the only mechanism operating.

The spectroscopic features of the oxazaphosph(v)oles were discussed in detail, in particular the variable temperature n. m. r. spectra of the 2-oxo-1,2,5-oxazaphosph(v)oles. These were discussed in terms of the pseudorotation processes taking place, and free energies of activation were calculated for the oxazaphosph(v)oles derived from dimethyl phenylphosphonite. The hindered rotation of a 1,2,5-oxazaphosph(v)ole was also studied.

The reactions of two 2-alkyl-1,2-diphenylnitroethenes with triethyl phosphite were investigated, and steric effects on the formation of 2-oxo-1,2,5-oxazaphosph(v)oles discussed. It was found that the high temperature reaction led to an unusual phosphite-induced rearrangement without deoxygenation of the nitro group.

The acid catalysed hydrolyses of the 2-oxo-1,2,5-oxazaphosph(v)-oles were studied. The results were interpreted in terms of competitive protonation of the N-oxide function and the apical methoxyl group. The principal products were ketone phosphonates arising via a Nef reaction. In one case where the phenyl ring contained a p-methoxyl group, a completely different reaction occurred resulting in the formation of a spirodienone.

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# A. Deoxygenation of Compounds Containing Nitrogen-Oxygen Bonds

## A. 1 General Considerations

A vast number of examples of the general reaction of tervalent organophosphorus compounds with compounds containing nitrogen-oxygen bonds have been known for some time.[1, 2] The phosphorus reagent may be, for example, a trialkyl- or triaryl-phosphine or phosphite, and typical oxygen-containing compounds are nitro and nitroso compounds,[2, 3, 4, 5] and amine N-oxides.[1, 6] The principal driving force behind these reactions is the great strength of the P=O bond in the oxygenated phosphorus products. The bond dissociation energies lie typically in the range 500-630 kJ $mol^{-1}$,[7] compared with 210-300 kJ $mol^{-1}$ for the $N^{+}$-$O^{-}$ bond in amine N-oxides.[8]

The following introductory sections A. 2 and A. 3 will focus attention on more specific examples of this general reaction (Scheme 1), including

$$:PR_3 + ZO \longrightarrow OPR_3 + Z$$

Scheme 1

the scope and limitations of the reaction as a synthetic tool, and mechanistic features of the deoxygenations.

## A. 2 Deoxygenation of N-Oxides

### (a) Deoxygenation of Heterocyclic N-Oxides

The conversion of heterocyclic N-oxides to the parent amine is a necessary part of the reaction sequence utilising the N-oxide to obtain substitution patterns not otherwise obtainable from the parent heterocycle.[9] A variety of phosphorus(III) reagents have been used to effect this conversion,

among them phosphorus trichloride,[6,10] phosphines,[11,12] and phosphites.[13,14]

Reduction of N-oxides by phosphorus trichloride has been studied in some detail. Ochiai[6] found that pyridine and quinoline N-oxides were smoothly deoxygenated to the corresponding amines by phosphorus trichloride in chloroform. There were, however, complications due to replacement by chlorine of nitro and hydroxyl groups in the 4-position of quinoline 1-oxides. For example, 4-nitroquinoline 1-oxide gave 4-chloroquinoline in 82% yield, and 4-hydroxyquinoline 1-oxide was deoxygenated to a mixture of approximately equal amounts of 4-hydroxy- and 4-chloroquinoline. Similarly, reduction of 3-isoquinolinecarboxylic acid 2-oxide with phosphorus trichloride also resulted in conversion of the carboxylic acid function to the acid chloride.[15]

In a kinetic study of N-oxide deoxygenation by $PCl_3$ in chloroform, Emerson and Rees[10] showed that the reaction was inhibited by traces of hydrogen chloride present in the phosphorus reagent. The rate was greatly increased by addition of 2,6-lutidine, which is a weak nucleophile but a stronger base than the N-oxides. The rate of deoxygenation of 3-nitropyridine 1-oxide was found to be too high to measure, whereas reduction of 4-nitropyridine 1-oxide was much slower. Comparison of the results for pyridine 1-oxide and 4-nitropyridine 1-oxide showed that electron withdrawal from the oxide group significantly decreases the reaction rate.[10] As in the case of protonation of the oxygen atom, this causes a decrease in the nucleophilicity of the oxygen atom. Under the same reaction conditions, 3,4-benzocinnoline 5-oxide and 5,6-dioxide did not react, nor did azoxybenzene.[10] The inertness of the 5-oxide is possibly due to dimer formation, which is also possible with azoxybenzene. The lack of reactivity of the

5,6-dioxide has been ascribed to resonance stabilisation.

It has been observed[16] that the ease of reduction of pyridine N-oxide by tervalent phosphorus reagents decreased in the series

$PCl_3 > PhPCl_2 > Ph_2PCl \gg (PhO)_3P > (EtO)_3P \ggg Ph_3P > Bu_3P > Et_2PPh.$

The activity of the phosphorus reagent is reduced by substituting the halogen atoms in $PX_3$. Electron-donating groups attached to phosphorus therefore diminish the activity. Together with the results referred to above,[10] namely that electron withdrawal from the oxide group decreases the reaction rate, this suggests that the mechanism of the deoxygenation involves nucleophilic attack of the N-oxide oxygen on the phosphorus reagent, which is acting as an electrophile. This is the opposite of the situation in the case of nitro and nitroso compounds, as will be seen later.

Phosphites have also been used to deoxygenate N-oxides. Interestingly, 3,4-benzocinnoline 5,6-dioxide can be deoxygenated in high yield by triethyl phosphite,[17] although not with phosphorus trichloride.[10] This is a curious result in view of the general order of reactivity discussed above,[16] and may suggest a different mechanism operating in this case. Reduction of pyridine N-oxide to pyridine has also been effected with triphenyl phosphite.[14] As is the case with phosphorus trichloride deoxygenations, complications can very occasionally arise in phosphite deoxygenations when the heterocyclic ring has labile substituents. For example, 2-nitropyridine N-oxide (but not the 4-isomer) is sufficiently activated to react with triethyl phosphite with displacement of the nitro group to give diethyl 2-pyridylphosphonate.[18]

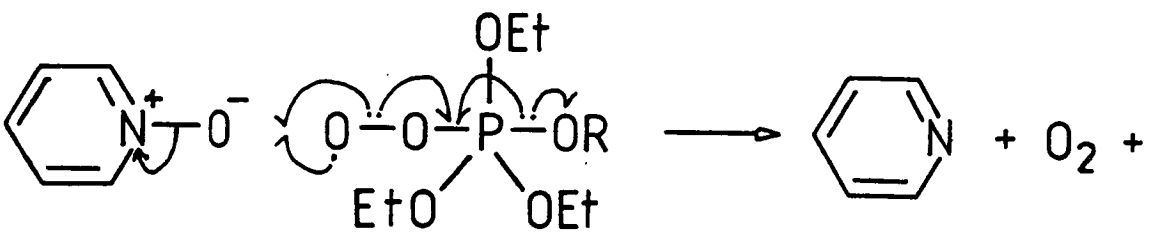
Emerson and Rees[13] found that pyridine N-oxide was deoxygenated at room temperature by triethyl phosphite in unpurified diethylene glycol diethyl ether. This appeared to be due to the presence of peroxides in the

solvent, and oxygen was also necessary. A mechanism involving a peroxy radical (1) has been suggested[13] (Scheme 2), although an alternative involving decomposition of the intermediate phosphoranyl radical (2) has also been proposed[19] (Scheme 3).

$$RO{\cdot}OR \rightleftharpoons 2\,RO{\cdot}$$

$$(EtO)_3P + RO{\cdot} \rightleftharpoons (EtO)_3\dot{P}(OR) \quad (2)$$

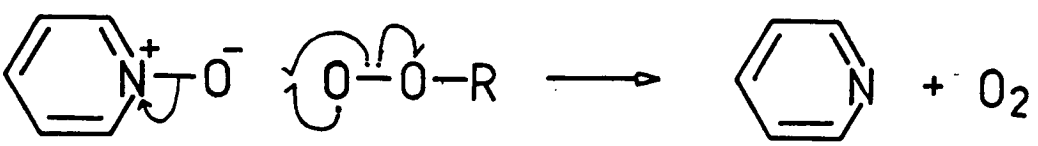
$$(EtO)_3\dot{P}(OR) + O_2 \rightleftharpoons (EtO)_3P(OR){\cdot}O{\cdot}O{\cdot} \quad (1)$$




Scheme 2

$$(EtO)_3\dot{P}(OR) \longrightarrow (EtO)_3PO + R{\cdot}$$

$$R{\cdot} + O_2 \longrightarrow ROO{\cdot}$$

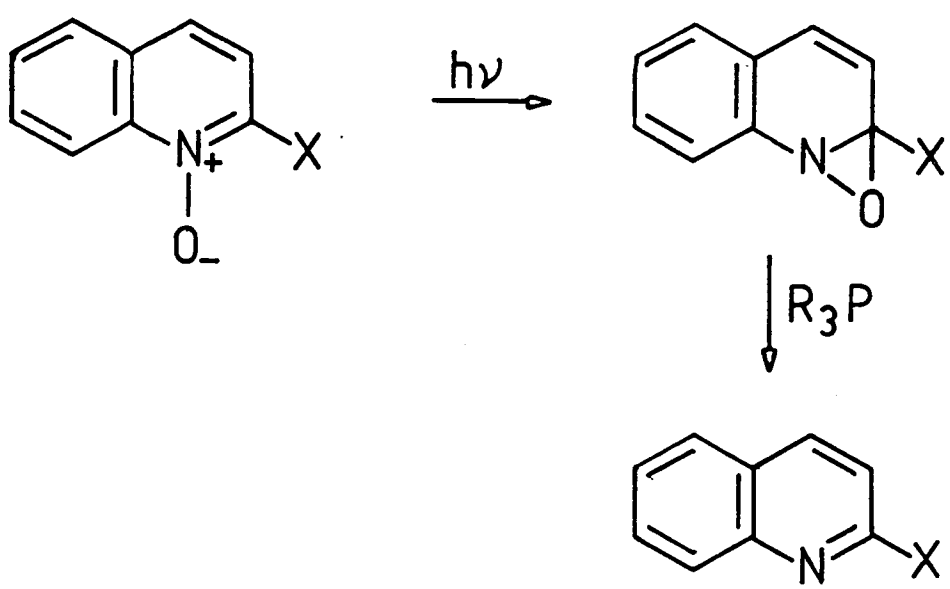



Scheme 3

In spite of their position on the scale of reactivity of phosphorus(III)

reagents in N-oxide deoxygenations,[16] phosphines have been successfully employed in such reactions. Reduction of trimethylamine oxide with triphenylphosphine gives trimethylamine quantitatively,[12] and similar reactions have been found with aromatic amine oxides at temperatures above 200°C.[11] Under these conditions, however, attempted deoxygenation of 4-nitropyridine N-oxide resulted in evolution of nitrous fumes, and the only product isolated was triphenylphosphine oxide.[11]

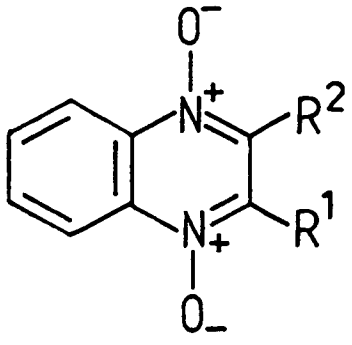
A relatively mild procedure for the deoxygenation of aromatic amine N-oxides has recently been described.[20] Irradiation of the N-oxides in dichlor methane in the presence of triphenylphosphine[20a] or trimethyl phosphite[20b] gave the parent amines in high yield. For example, 6-cyanophenanthridine 5-oxide gave 6-cyanophenanthridine in 95% yield. This procedure is probably not a true N-oxide deoxygenation as it is thought to proceed via an oxaziridine intermediate (Scheme 4).




Scheme 4

(b) Mono-deoxygenation of Heterocyclic Di-N-Oxides

Mono-deoxygenation of di-N-oxides has proved possible in a number of cases, although the literature appears to deal almost entirely with quinoxalines (3).



(a) $R^1 = CO.NMePh$ ; $R^2 = H$

(b) $R^1 = NHCO_2R$ ; $R^2 = H$

(c) $R^1 = CO_2CH_3$ , $COCH_3$ ; $R^2 = CH_3$

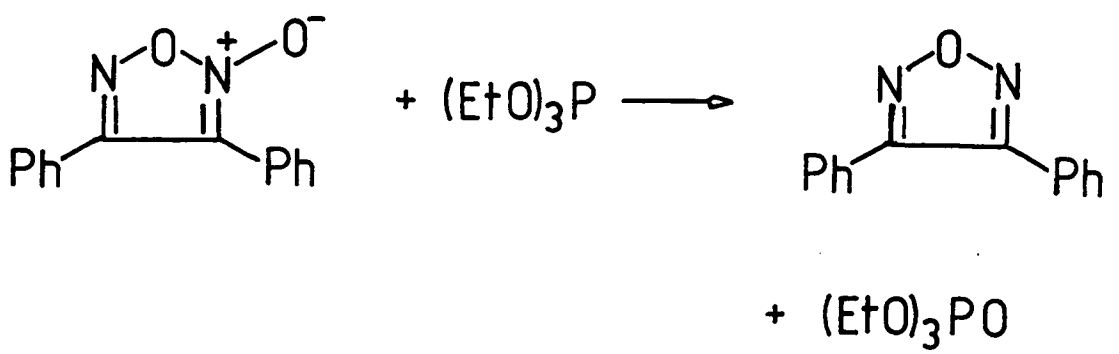
(3)

A study of the oxides of quinoxaline-2-carboxy-N-methylanilide showed that the 4-oxide could be reduced by phosphorus trichloride and the dioxide (3a) was reduced to the 1-oxide.[21] Further deoxygenation of the 1-oxide by $PCl_3$ was not possible, however. It was suggested that this is due to steric hindrance caused by the bulky 2-substituent. Similarly, methyl and ethyl quinoxalin-2-ylcarbamate 1,4-dioxide (3b) were deoxygenated by phosphorus trichloride to the 1-oxide.[22] A more recent study[23] has shown that deoxygenation of the 2,3-disubstituted quinoxaline 1,4-dioxides, 2-carbomethoxy- and 2-acetyl-3-methylquinoxaline 1,4-dioxide (3c), with phosphorus trichloride leads to the formation of both possible mono-N-oxides, as well as a significant amount of the fully deoxygenated quinoxaline. Changing to trimethyl phosphite in refluxing propan-1-ol, however, resulted in the formation of the 4-N-oxide as the sole product. Additionally, reaction

of 2-trifluoromethyl-3-methylquinoxaline 1,4-dioxide with trimethyl phosphite gave only the 4-oxide. In refluxing propanol, there is of course the possibility of transesterification and so the effective deoxygenating agent may not be trimethyl phosphite. Quinoxaline 1,4-dioxides without an electron-withdrawing group adjacent to the N-oxide function do not undergo deoxygenation with trimethyl phosphite.[23] An unexpected result was obtained on reduction of quinoxaline-1,4-dioxide-2-aldehyde, the product being the corresponding carbinol without deoxygenation of the N-oxide functions.[23] The expected quinoxaline-1-oxide-3-aldehyde can be obtained by rearrangement of the alcohol with acid.

(c) Deoxygenation of Furoxans and Furazans

Simple furoxans can be fairly readily deoxygenated to furazans. For example, reaction of diphenylfuroxan with triethyl phosphite at 160-170°C for 5 h gave diphenylfurazan and triethyl phosphate in high yield[24] (Scheme 5).




Scheme 5

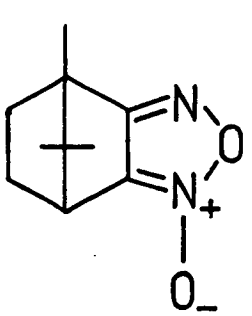
Grundmann[25] showed that a variety of furoxans were deoxygenated to furazans by trialkyl- or triarylphosphines and trialkyl phosphites. He studied the electronic effect of substituents on the furoxan ring and found

that electron-withdrawing groups tended to facilitate the reaction, while an electron-donating or aryl group had the opposite effect. No definite trends in the effect of changing the phosphine or phosphite were apparent, although tributylphosphine was remarkably effective at reducing diphenylfuroxan.

Complications sometimes arise during furoxan deoxygenation due to cleavage of the furazan ring, leading to nitriles as the final product. Diphenylfuroxan reacts with triphenyl phosphite at 270°C to give benzonitrile in 87% yield.[26]

Simple fused furoxans are also readily reduced.[17, 27] 5-Chlorobenzofuroxan, for example, was reduced to the corresponding furazan (60%) after 0.5 h with triethyl phosphite in refluxing ethanol.[27] Fusion of more complex ring systems to the furoxan ring can have a quite major effect on the ease of the reduction and/or the course of the reaction. In contrast to the simple fused furoxans, phenanthrofuroxan is recovered unchanged after 7 h at 112°C with trimethyl phosphite, although the higher boiling triethyl phosphite converts it almost quantitatively to the furazan.[28]

Bornenofuroxan (4), on the other hand, did not give the furazan on deoxygenation with trimethyl phosphite, but instead gave camphoronitrile.[28] Similarly, acenaphtho[1, 2-c]furazan-1-oxide (5) was converted to naphthalene-



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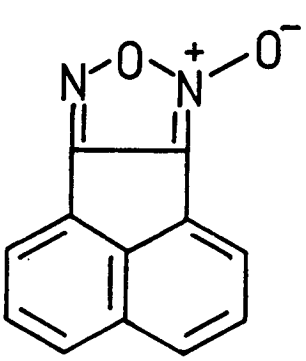
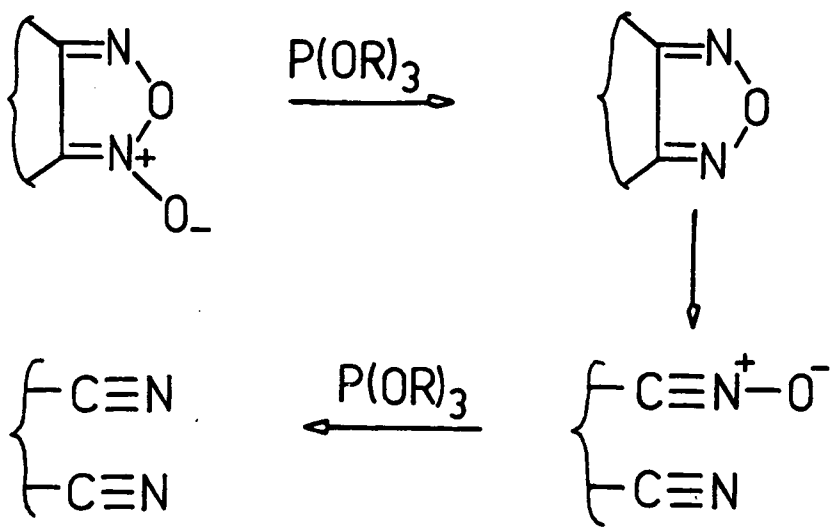


(5)

1, 8-dicarbonitrile. In both these cases where a five-membered ring is fused to the furoxan ring, the reaction conditions are much milder than those usually employed to effect the conversion of furoxan to furazan. On the basis of the available evidence, a mechanism (Scheme 6) has been proposed involving an intermediate furazan which ring-opens to the nitrile-nitrile oxide, which further deoxygenates to the dinitrile.[28] The ring-



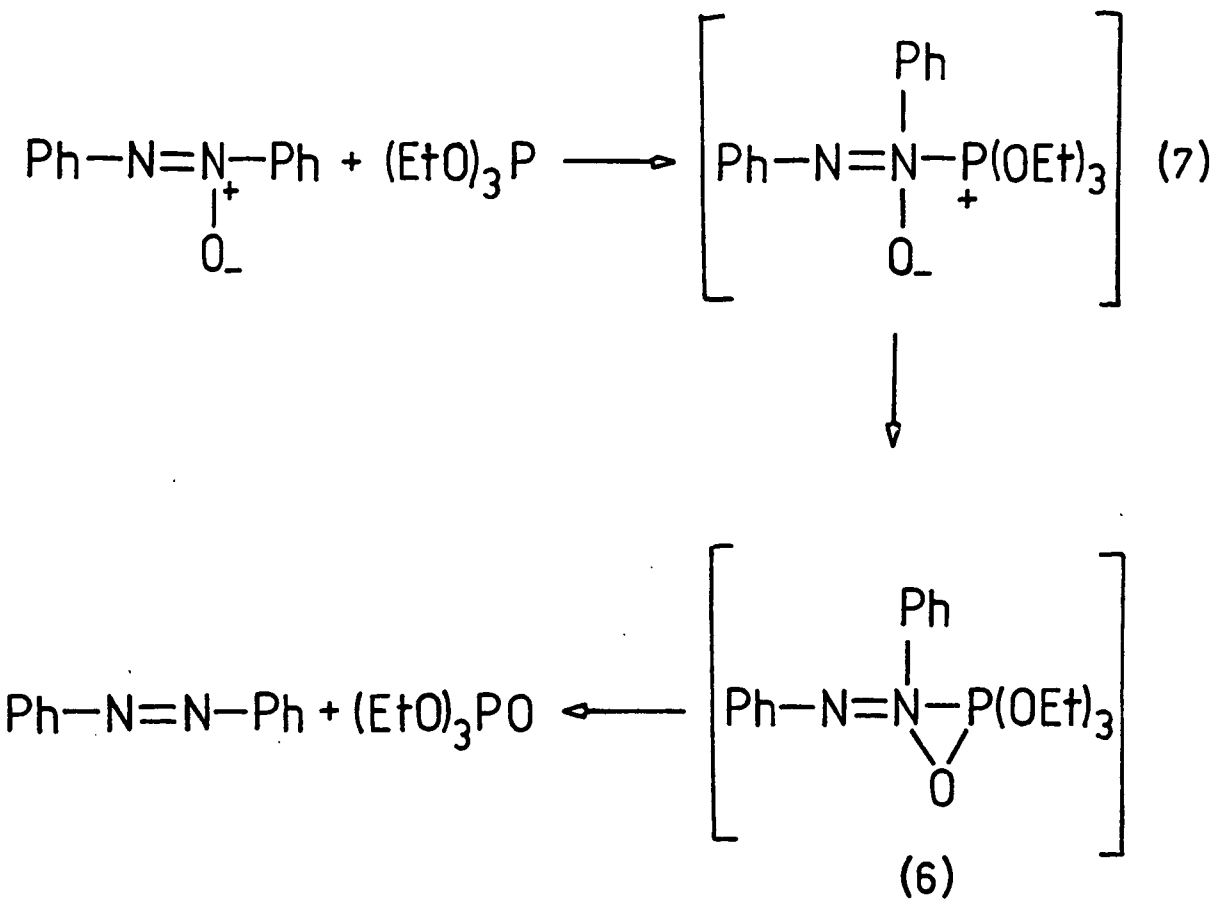

Scheme 6

opening is due to the strain experienced by the heterocyclic C-C bond due to fusion to a five-membered ring.

This ring-opening and subsequent deoxygenation of fused furazans can be accomplished at room temperature by irradiating with ultra-violet light in the presence of triethyl phosphite.[29] For example, benzofurazan gave principally Z - Z -1, 4-dicyanobuta-1, 3-diene with only small amounts of the other isomers. The preferential formation of one isomer is ascribed to a filtering effect of the solvent benzene, the chromophore of which coincides with that of the product, thus preventing photochemical isomerisation.

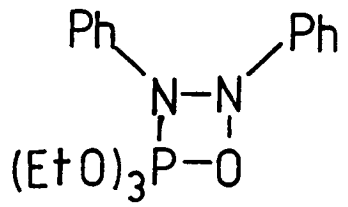
(d) Deoxygenation of Azoxy Compounds

Azoxybenzene can be deoxygenated by triethyl phosphite to give azobenzene in high yield.[17, 24] A mechanism involving an unlikely-looking three-membered ring intermediate (6) has been proposed[24] (Scheme 7).




Scheme 7

Nucleophilic attack by phosphite on the N-oxide nitrogen leads to the intermediate dipolar structure (7), which then ring closes to (6). An alternative mechanism has also been suggested via nucleophilic attack of the N-oxide oxygen on the phosphite.[24] There is also another possible mechanism which is much more feasible than that shown in Scheme 7. This would require nucleophilic attack at the other nitrogen atom and would result in the much more likely cyclic intermediate (8).



(8)

Azoxybenzene does not react with triphenylphosphine, but does so with triethylphosphine at 150°C to give a nearly quantitative yield of azobenzene.[12] Although azoxybenzene is inert towards phosphorus trichloride in chloroform,[10] it does deoxygenate almost quantitatively in refluxing $PCl_3$.[30]

A mild procedure for the deoxygenation of azoxy compounds to azo compounds in high yield (>90%) has recently been reported.[31] This simply involves refluxing the azoxy compound with tris(dimethylamino)phosphine/iodine/sodium iodide in acetonitrile.

(e) Deoxygenation of Nitrones

Aldonitrones are reduced by tertiary phosphines to the corresponding Schiff's bases in high yield.[12] Diphenylnitrone has been deoxygenated to the imine by trimethyl phosphite at 140-150°C, and with tris(dimethylamino)-phosphine.[32] The reaction has been extended to a steroidal nitrone which can be reduced in high yield to the imine with trimethyl phosphite.[33]

(f) Deoxygenation of Nitrile Oxides

Nitrile oxides can be reduced to the corresponding nitrile by reaction with trialkyl- or triarylphosphines and trialkyl phosphites.[34, 35] The choice of phosphorus reagent is determined purely by ease of product isolation.[35] Trimethyl or triethyl phosphite is used for water insoluble nitriles, and triphenylphosphine for water soluble nitriles.

## A. 3 Deoxygenation of Nitro and Nitroso Compounds

Much of the work described in this thesis concerns the reactions of 1, 2-diaryl-1-nitroethenes (*α*-nitrostilbenes), and for this reason a large part of this introductory section is devoted to deoxygenation reactions of nitrostyrenes and related compounds. This is followed by an abbreviated account of deoxygenation reactions of other nitroso and nitro compounds, and finally a short description of some synthetic applications of the reaction.

### (a) Deoxygenation of Nitrostyrenes and Related Compounds

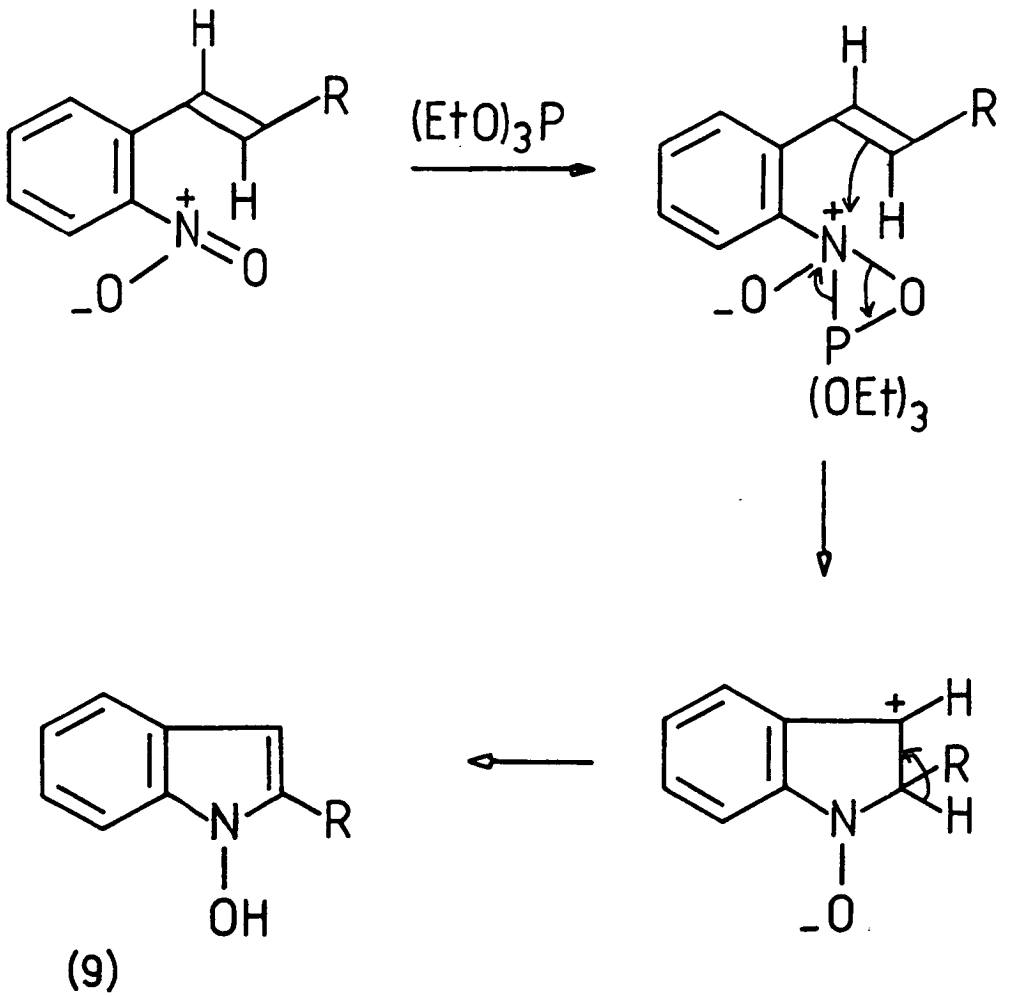
Cadogan and co-workers[36, 17] have shown that triethyl phosphite deoxygenation of cis- and trans-2-nitrostilbene gives 2-phenylindole in 85% and 58% yield respectively. Similarly, *α*-nitrostilbene gave 2-phenylindole on deoxygenation but the yield was only 16%.[17] These reductions were thought to be sensitive to steric environment. In support of this conclusion, it was found that 2-nitrostyrene gave only a trace of indole, β-nitrostyrene gave none at all, and o-nitrocinnamic acid gave a 7.5% yield of ethyl indole-2-carboxylate.[17]

As a continuation of his work on indoles, Sundberg has carried out an extensive investigation of the reductive cyclisation reaction leading to indoles.

He found[37] that 2-alkylindoles could be obtained in ca 50% yield by reduction of β-alkyl-o-nitrostyrenes, but the corresponding acylindoles were obtained in much lower yield. An attempt to increase the yield by first forming the ketals of the β-acyl-o-nitrostyrenes resulted in no significant improvement.[38] In addition, fragmentation and rearrangement products were formed.

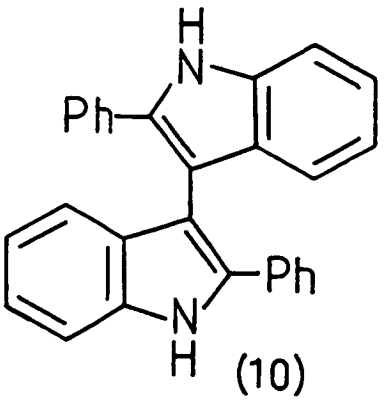
Sundberg[37] has suggested a mechanism for the reductive cyclisation,

involving ring closure prior to total deoxygenation of the nitrogen atom (Scheme 8). This would entail the intermediacy of 1-hydroxyindoles (9).




Scheme 8

It was found that deoxygenation with triethyl phosphite of trans-o-nitrostilbene and 1-hydroxy-2-phenylindole gave exactly the same products, viz 2-phenylindole (major product), 2, 2'-diphenyl-3, 3'-biindolyl (10), and diethyl 2-phenyl-3-indolylphosphonate (11). As final evidence for its intermediacy, 1-hydroxy-2-phenylindole was isolated in 15% yield from a deoxygenation interrupted before completion. 1-Ethoxyindoles were also obtained as by-products in some of the nitrostyrene reactions, but never



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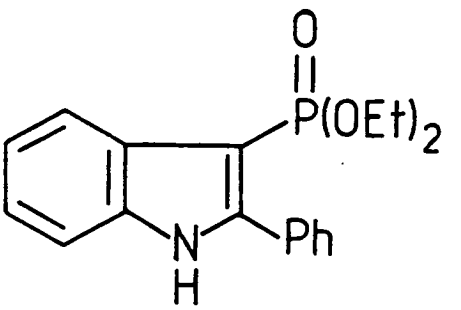
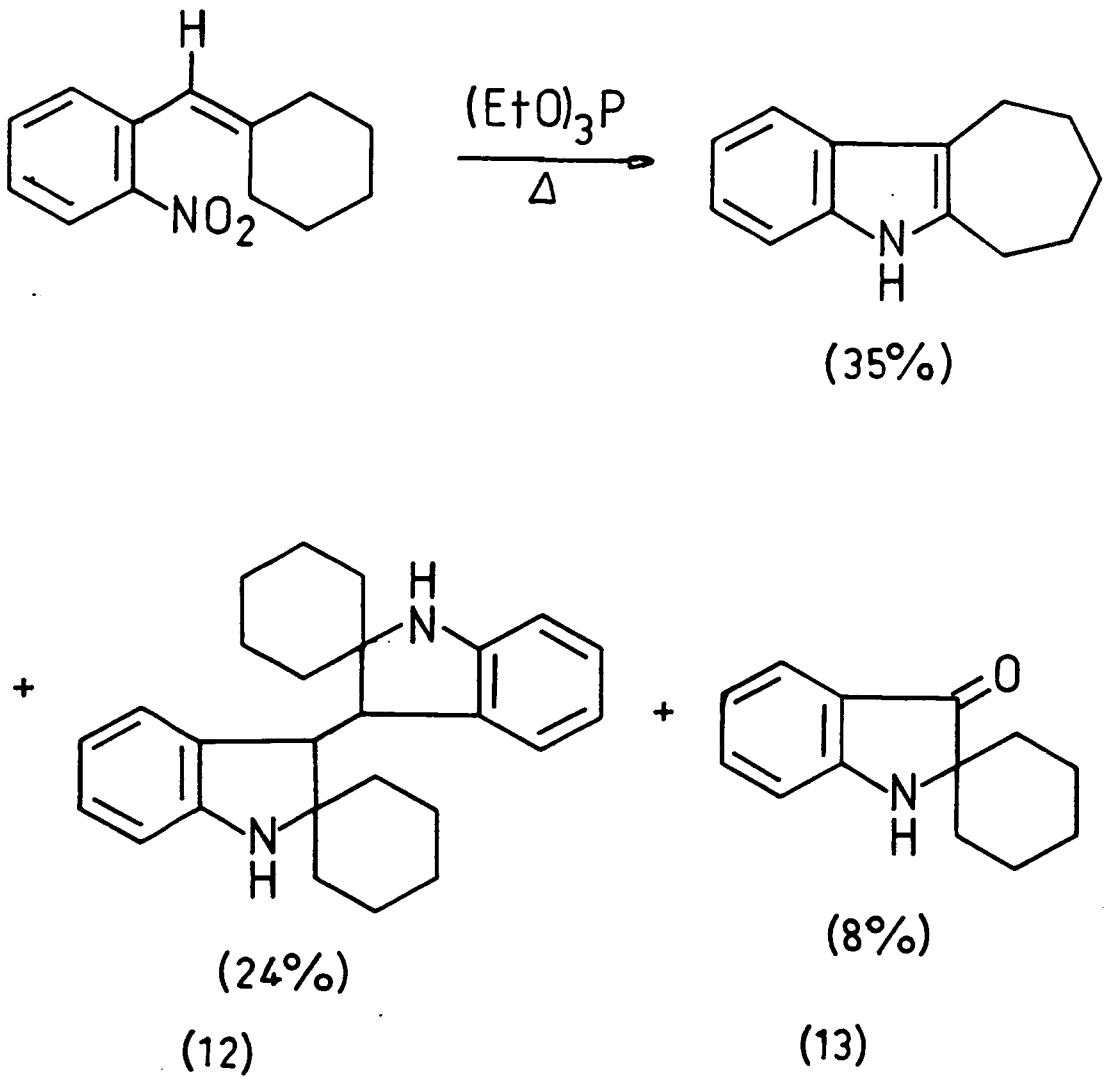


(11)

from the o-nitrostilbenes.[37]

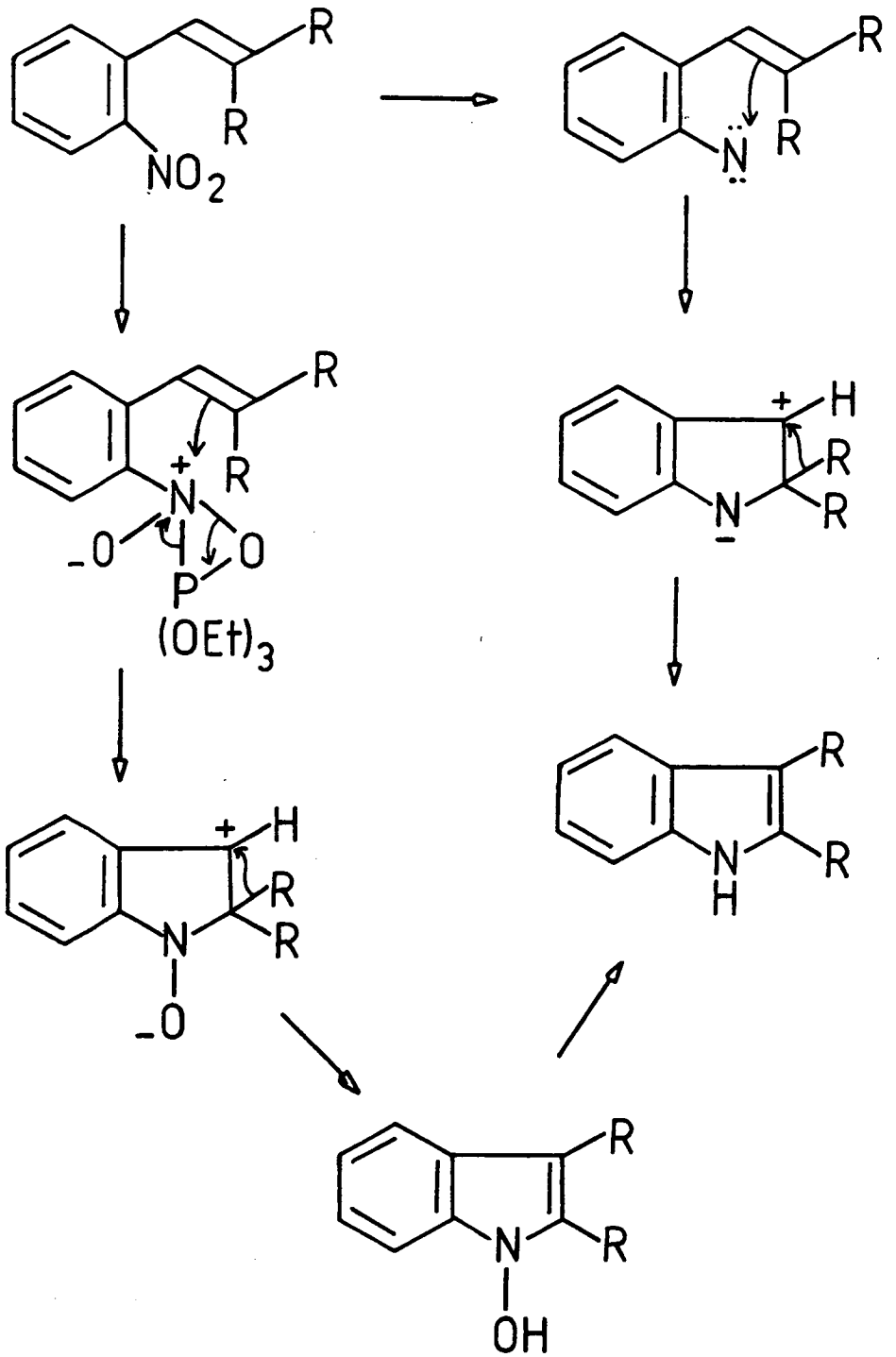
The yield of the biindolyl was increased when the concentration of triethyl phosphite was reduced, indicating that some intermediate is being diverted to the biindolyl. However, the product yields were not high enough for it to be stated with certainty that the substance being diverted to the biindolyl is converted to 2-phenylindole in excess triethyl phosphite, although it seems likely that this is the case.[37]

In a study of the deoxygenation of β,β-disubstituted o-nitrostyrenes, it was found that the rearranged 2,3-disubstituted indole was formed in every case (e. g. Scheme 9).[39] Minor products were the biindolinyl (12) and the indolinone (13). Similar deoxygenation of β,β-dimethyl-o-nitrostyrene gave 2,3-dimethylindole (33%), the indolinone (11%), and a very low yield of the biindolinyl. Trans-α-methyl-2'-nitrostilbene, which has two possible migrating groups, gave 1-ethyl-2-methyl-3-phenylindole (21%) and 2-methyl-3-phenylindole (77%). The 1-ethyl derivative is presumably formed via ethylation with triethyl phosphate. The preferential phenyl migration is expected for migration to a cationic centre,[40] but the



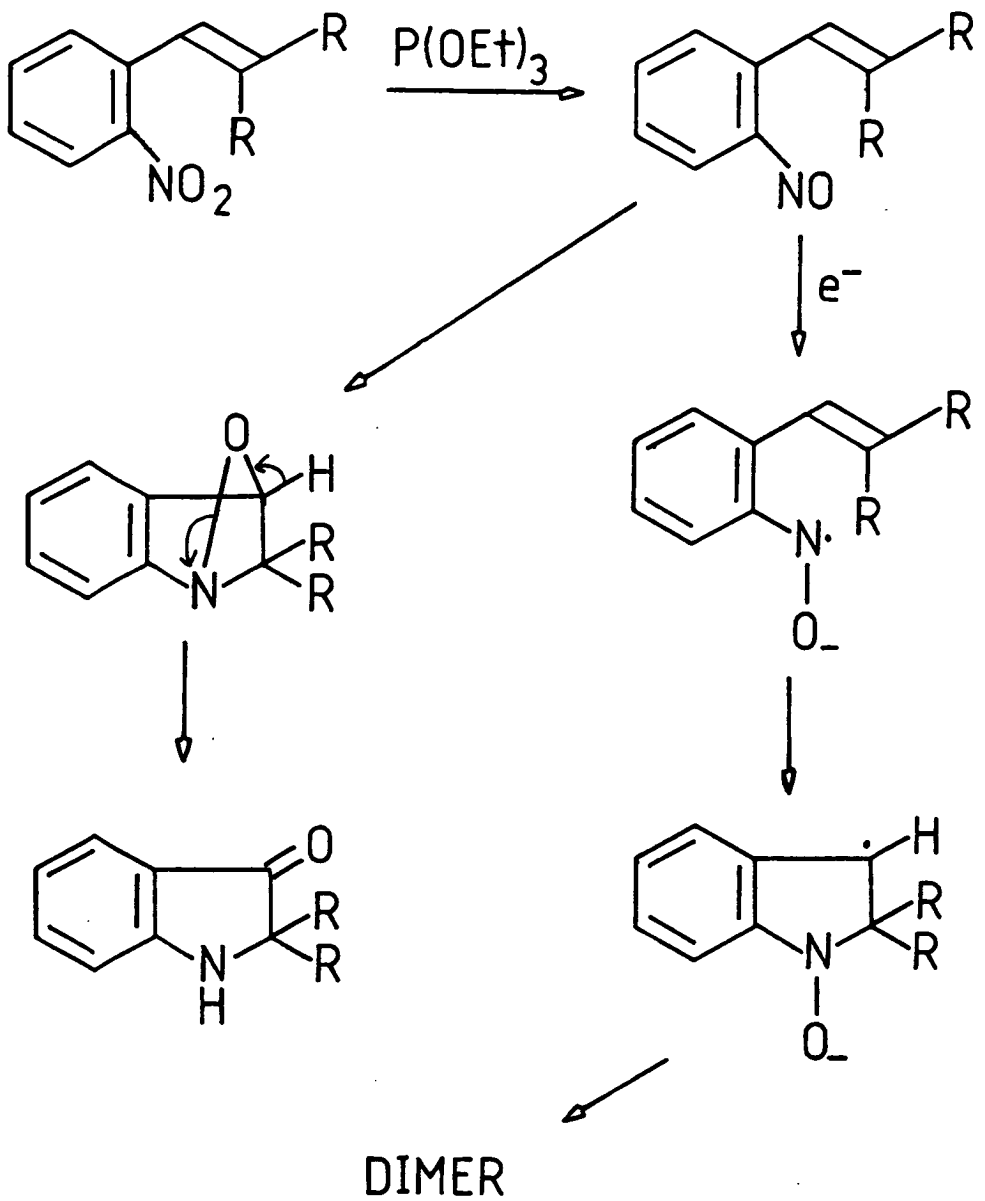

Scheme 9

stereochemical configuration of the nitrostilbene may also have an effect. The rearrangement would fit with either the nitrene mechanism or the hydroxyindole mechanism (Scheme 10), although no hydroxyindoles could be isolated from interrupted deoxygenations.



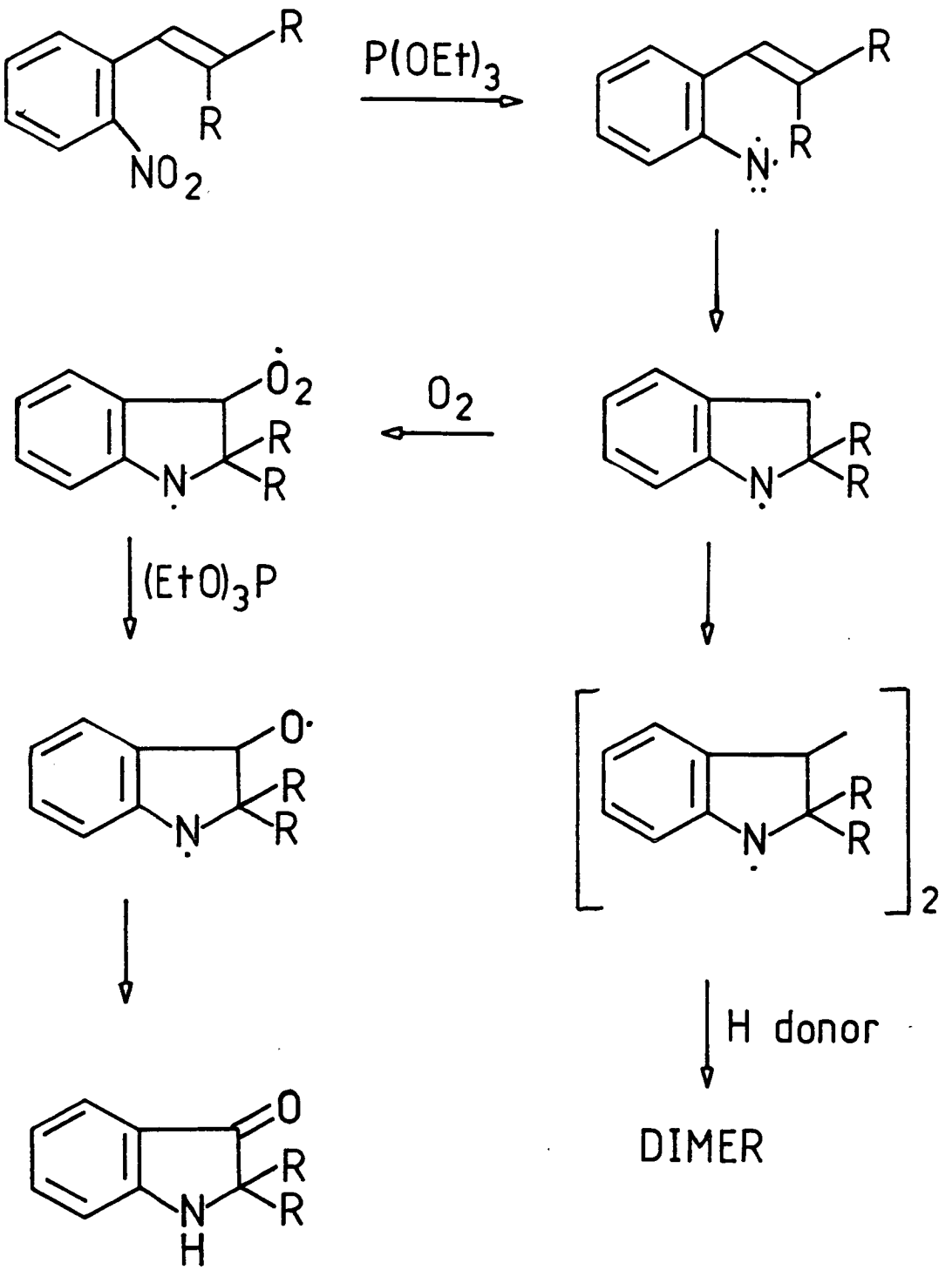
Scheme 10

There is a great deal of uncertainty concerning the origin of the by-products. Sundberg[39] has put forward a tentative mechanism involving radical formation via the nitroso compound (Scheme 11).




Scheme 11

An alternative mechanism, proceeding via the triplet nitrene, has been suggested by Cadogan[2] (Scheme 12).

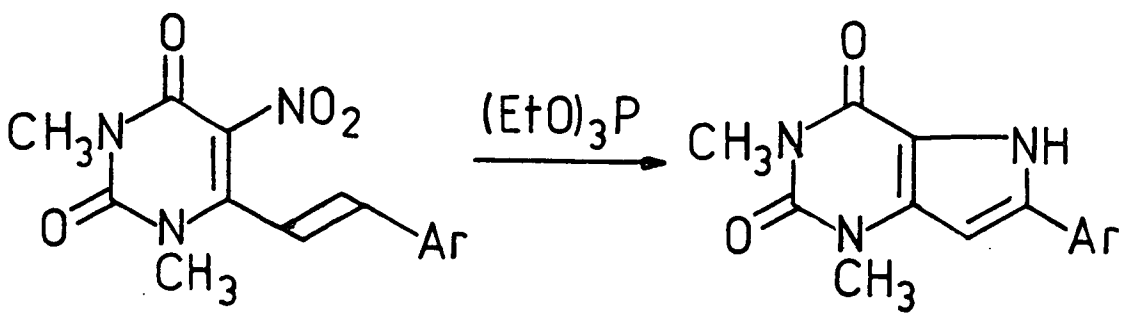



Scheme 12

Phenylacetonitrile has been obtained both from the deoxygenation of β-nitrostyrene with triethyl phosphite, and from the photolysis of β-styryl azide.[41] This has led to the suggestion that β-styryl nitrene may

be a common intermediate. It has also been reported that the deoxygenation reaction gives a compound showing a positive indole test.[42b]

In addition to the mechanistic studies detailed above, synthetic use has been made of the deoxygenation reaction of nitrostyrenes. Taylor and Garcia[43] prepared the pyrrolo[3, 2-d]pyrimidines (14) in low yield by thermal and photochemical deoxygenation of the 5-nitro-6-styryluracils (15) with triethyl phosphite (Scheme 13).

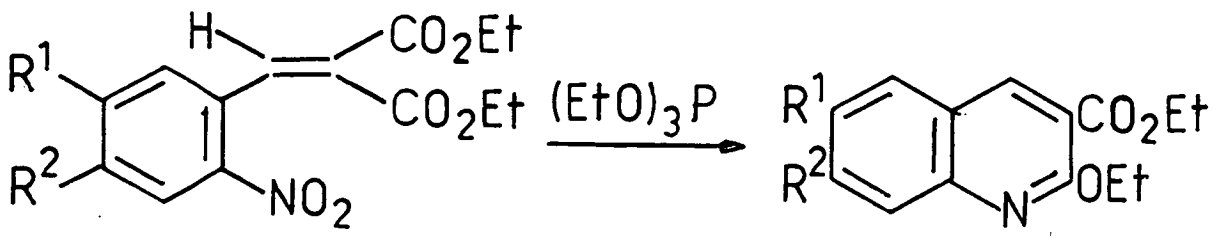



(15) (14)

Ar = p−$CH_3OC_6H_4$ ; p−$(CH_3)_2NC_6H_4$ .

Scheme 13

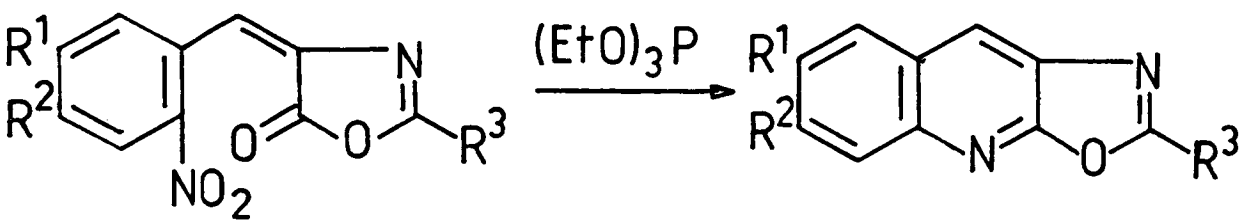
Kametani[44] has shown that reaction of ethyl 2-nitrobenzylidene-malonates with triethyl phosphite affords a novel synthesis of quinolines (Scheme 14). Quinolines were again obtained in moderate yield from the reaction of 2-substituted-4-(4, 5-dialkoxy-2-nitrobenzylidene)oxazol-5-ones with triethyl phosphite[45] (Scheme 15). Three possible routes to these oxazolo-[5, 4-b]quinolines have been suggested.




(a) $R^1 = R^2 = OCH_3$

(b) $R^1 = OCH_3$ , $R^2 = OCH_2Ph$

Scheme 14




(a) $R^1 = R^2 = OCH_2O$ ; $R^3 = Ph$

(b) $R^1 = R^2 = OCH_2O$ ; $R^3 = Me$

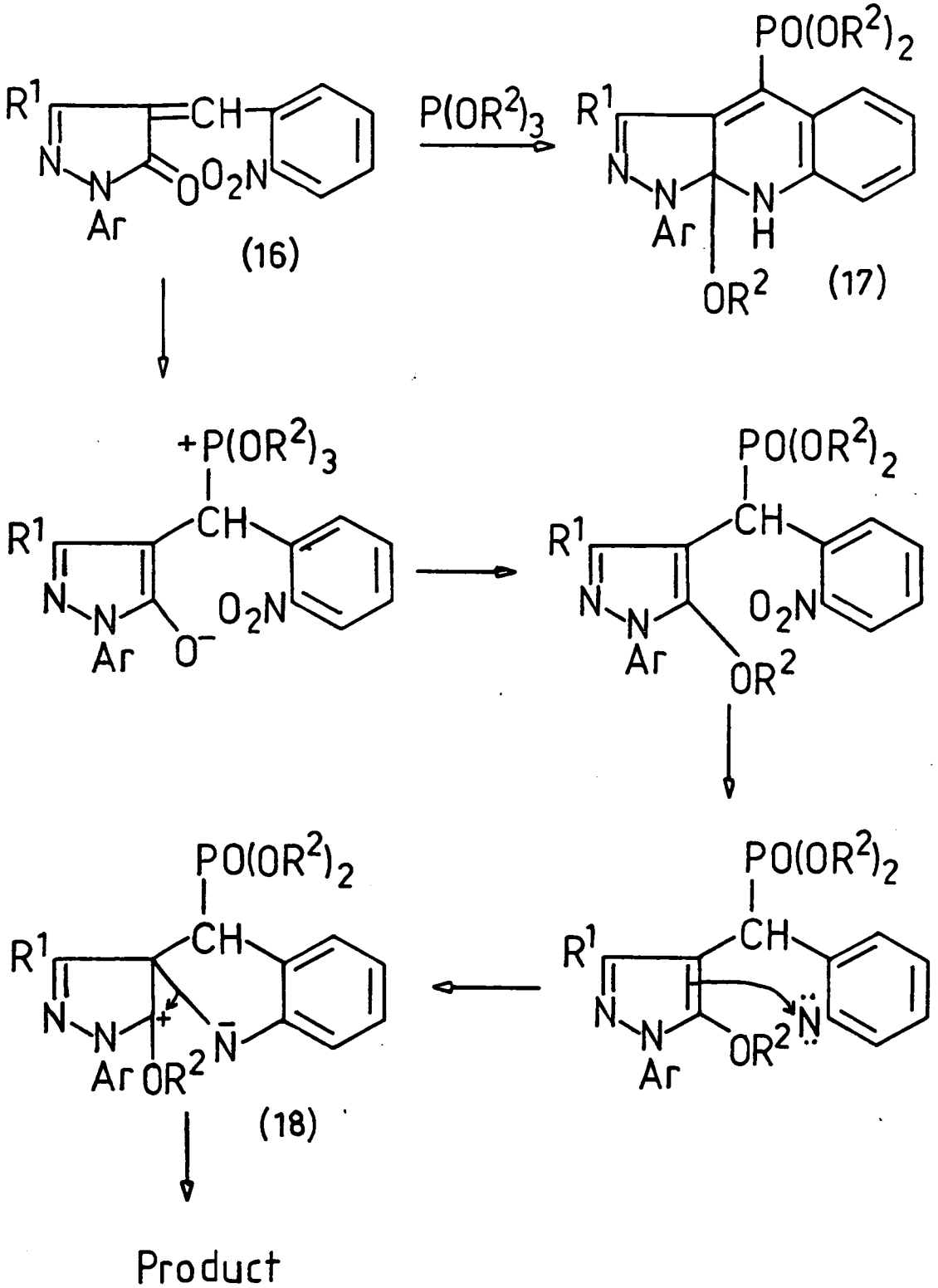
(c) $R^1 = R^2 = OMe$ ; $R^3 = Ph$

(d) $R^1 = R^2 = OMe$ ; $R^3 = Me$

Scheme 15

Deoxygenation of the structurally similar 4-o-nitrobenzylidene-$\Delta^2$-

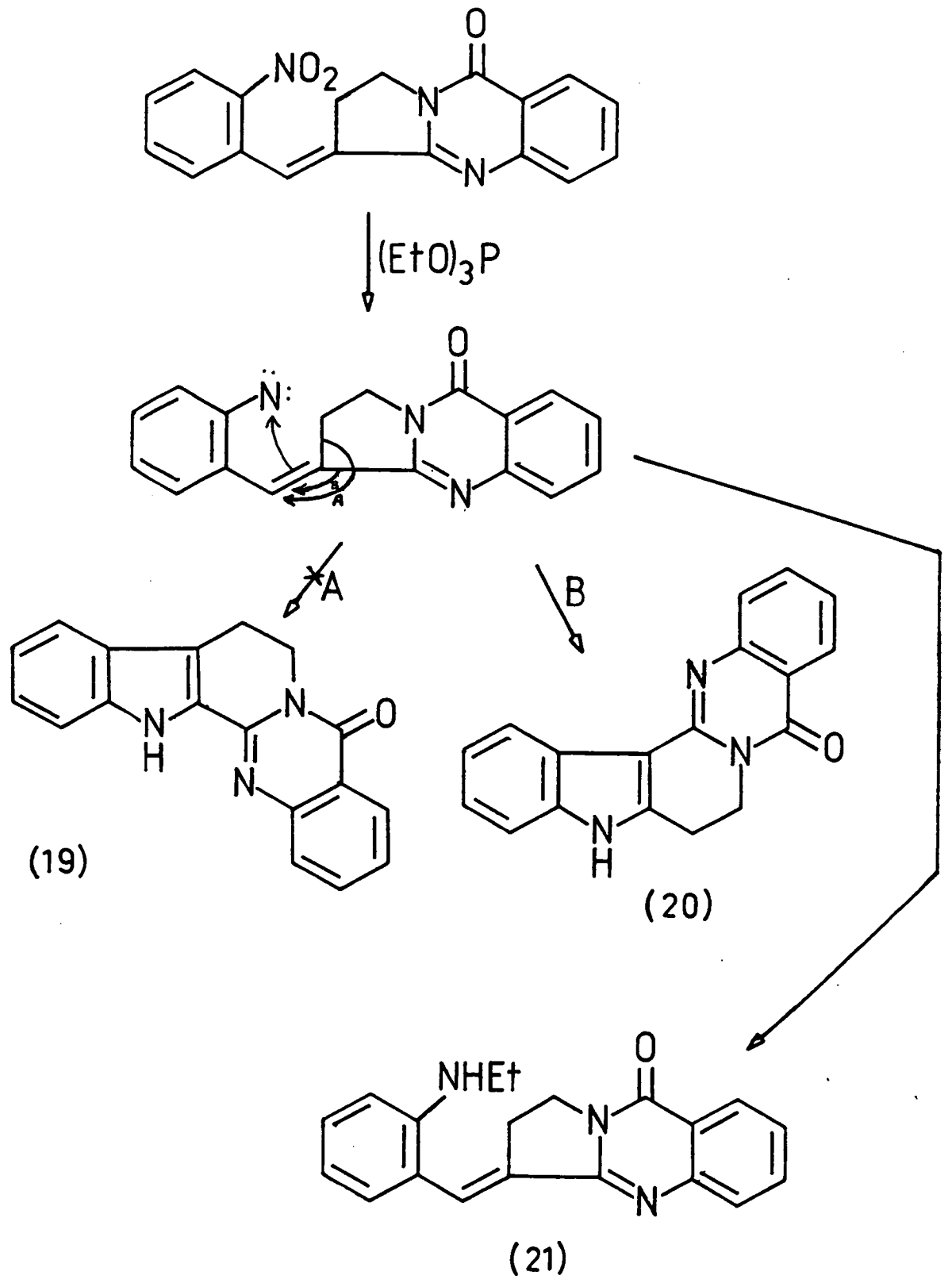
pyrazolin-5-ones (16) with trialkyl phosphites generally gave dialkyl 9a-alkoxy-9, 9a-dihydropyrazolo[3, 4-b]quinolin-4-ylphosphonates (17) as the major products (7-25%).[46] The proposed mechanism (Scheme 16) involves




Scheme 16

a spiro-intermediate (18).

Kametani[47] has attempted to use the method of Sundberg,[39] involving ring closure and rearrangement of β,β-disubstituted o-nitrostyrenes, in a

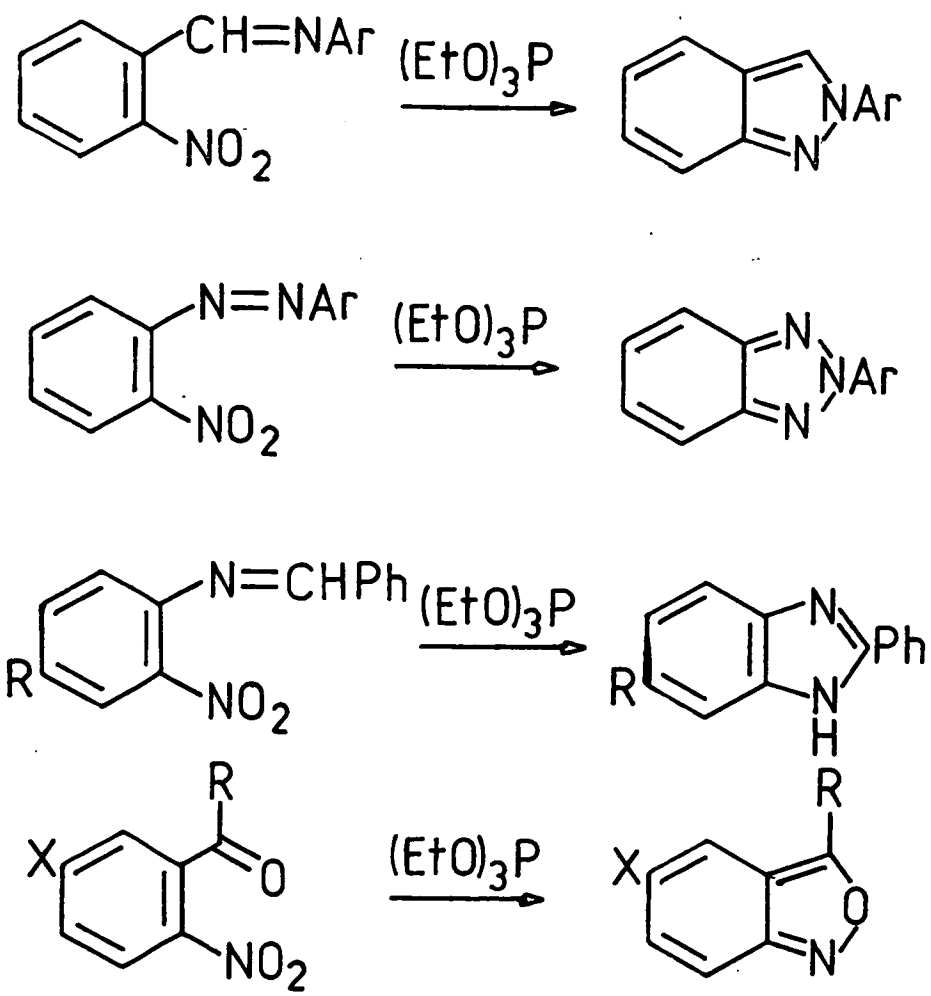



Scheme 17

synthesis of the indole alkaloid rutaecarpine (19). Unfortunately, the alternative substituent migrated (route B) giving a product which Kametani called pseudorutaecarpine (20), in addition to the aniline derivative (21) (Scheme 17).

Extensions of the reactions described above have also been reported.[48, 4

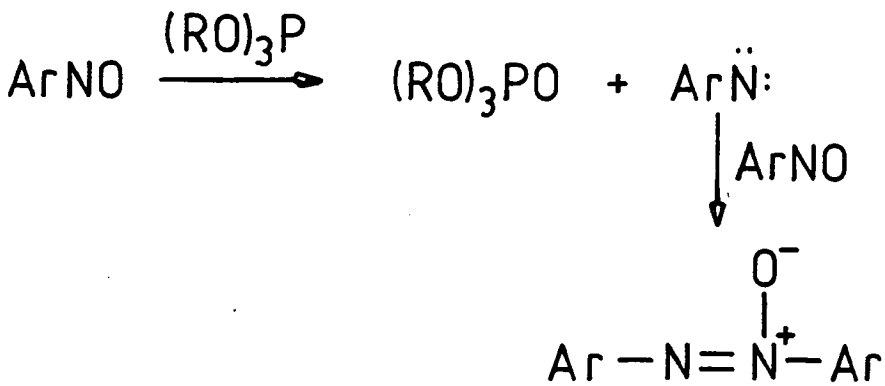
The cyclisation reaction can be extended to other systems formally related to the nitrostyrenes by replacement of one or both carbon atoms in the double bond by a heteroatom. Thus, 2-nitroanils and 2-nitroazobenzenes can be reduced to 2-arylindazoles and 2-arylbenzotriazoles respectively,[17, 50] and similar reactions can be used to prepare benzimidazoles and anthranils[51] (Scheme 18).




Scheme 18

(b) Deoxygenation of Nitroso Compounds

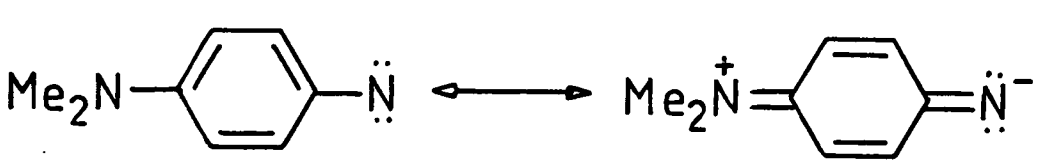
The first report of such a reaction was the discovery by Horner and Hoffmann[12] that substituted nitrosobenzenes reacted with triphenylphosphine to give a moderate yield of the corresponding azoxybenzenes. Bunyan and Cadogan[52] obtained a low yield of azoxybenzene from reaction of triethyl phosphite with nitrosobenzene itself. They also obtained a 76% yield of carbazole from deoxygenation of 2-nitrosobiphenyl, and from this they inferred the intermediacy of a nitrene. The formation of azoxybenzene has also been explained by a nitrene mechanism[53] (Scheme 19).




Scheme 19

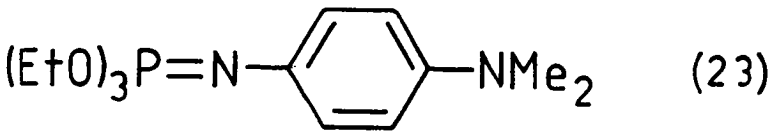
The nitrene from o-ethylnitrosobenzene might be expected to give the dihydroindole *via* insertion into the ethyl side chain, but this does not happen. This apparent anomaly is explained by the ease of reaction of the nitrene with unchanged nitroso compound being greater than the ease of insertion.[53]

The use of N, N-dimethyl-p-nitrosoaniline should lead to a more stable nitrene (22), and therefore less reaction with the nitroso group. It




(22)

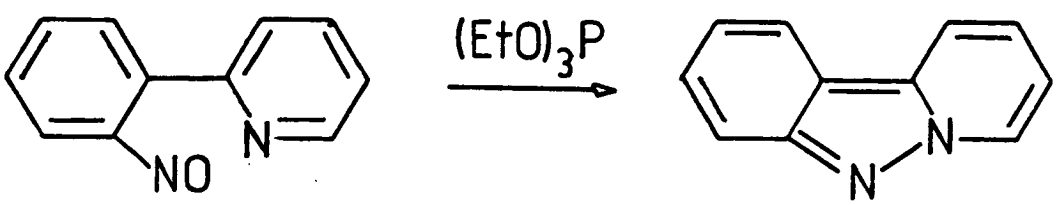
was found that deoxygenation of this nitroso compound gave a mixture of the azoxy compound and the phosphorimidate (23).[53] As the amount of



(23)

triethyl phosphite was increased, the proportion of phosphorimidate increased relative to the azoxy compound. This result is what would be expected for nitrene participation.

Deoxygenation of 2-o-nitrosophenylpyridine gave an almost quantitative yield of pyrid[1, 2-b]indazole[53] (Scheme 20). This is also consistent with

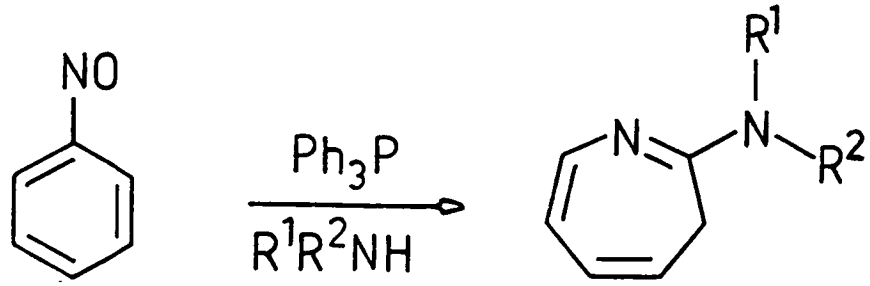


Scheme 20

the intermediacy of an electron-deficient nitrogen species, which would react preferentially at the electron-rich ring nitrogen atom.

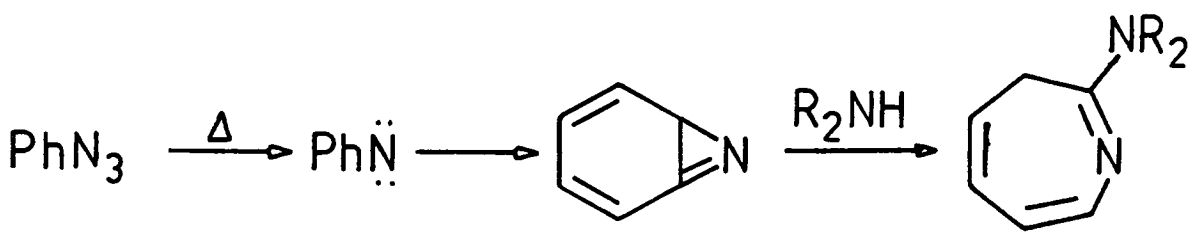
Further evidence for nitrenes has come from deoxygenation reactions carried out in the presence of amines. Deoxygenation of nitrosobenzene with triphenylphosphine or tributylphosphine in amine solvents resulted in the formation of the N-alkyl derivatives of 2-amino-3H-azepines[54] (Scheme 21).

Similar products have been reported for the photolysis[55] and thermolysis[56, 57] of phenyl azide in amines, a reaction involving nitrenes. It has been proposed[57] that 7-azabicyclo[4, 1, 0]hepta-2, 4, 6-triene (24)




Scheme 21

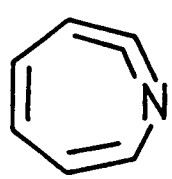
is an intermediate in the thermolysis reaction (Scheme 22). There is also




(24)

Scheme 22

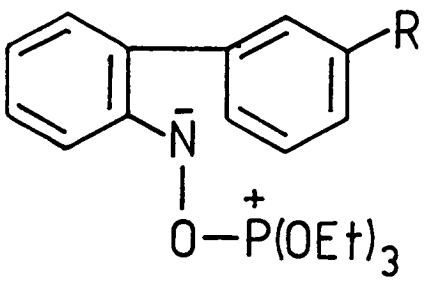
recent evidence[58] suggesting the intermediacy of 1-aza-1, 2, 4, 6-cyclo-heptatetraene (25) in the photolytic process. Either or both of these might




(25)

also be intermediates in the deoxygenation reaction.

A study of the thermal cyclisation of 3'-substituted 2-azidobiphenyls and deoxygenative cyclisation of the corresponding nitroso compounds has been made using deuterium labelling.[59] In this case, the results showed that the likely intermediate in the deoxygenation is a bipolar species (26) and not a discrete nitrene.



(26)

(c) Other Nitro Deoxygenations

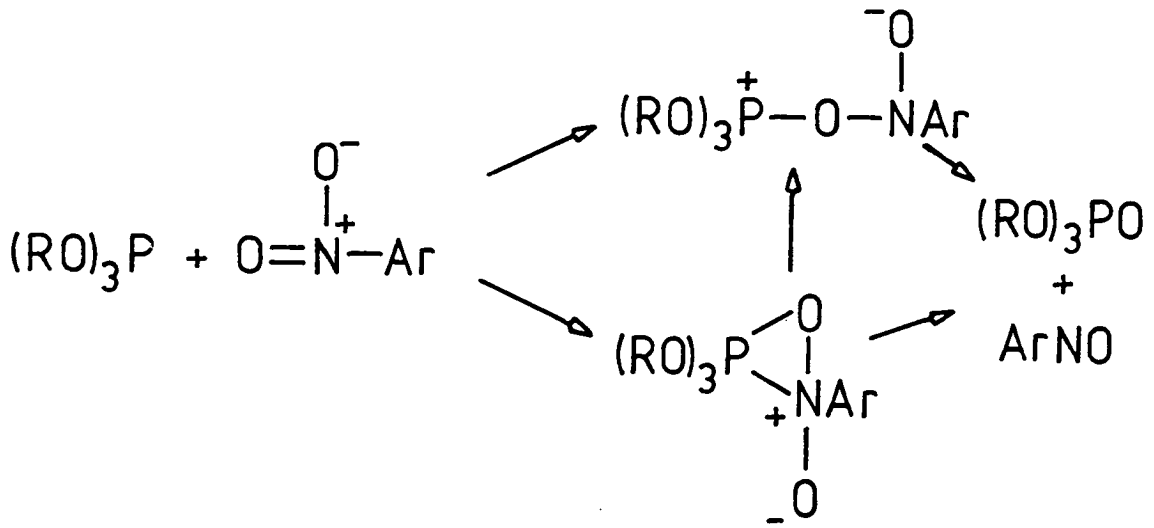
In a similar reaction to that of 2-nitrosobiphenyl,[52] it has been found that 2-nitrobiaryls also react with triethyl phosphite to give high yields of carbazoles.[36,17] Likewise, 2-o-nitrophenylpyridine was reduced to pyrido[1, 2-b]indazole in near quantitative yield[36] (cf. Scheme 20).

In a study of the deoxygenation of 2-nitrobiphenyl, it was found that the order of reactivity of the phosphorus reagent towards nitro deoxygenation decreased in the order[5,60]

$(Me_2N)_3P > (Et_2N)_3P \approx Ph_2POEt \approx (EtO)_2PMe > EtOP(NEt_2)_2 > (EtO)_2PNEt_2 > (MeO)_3P > (EtO)_3P \approx (Pr^iO)_3P > Ph_3P >>> PCl_3$ (inactive).

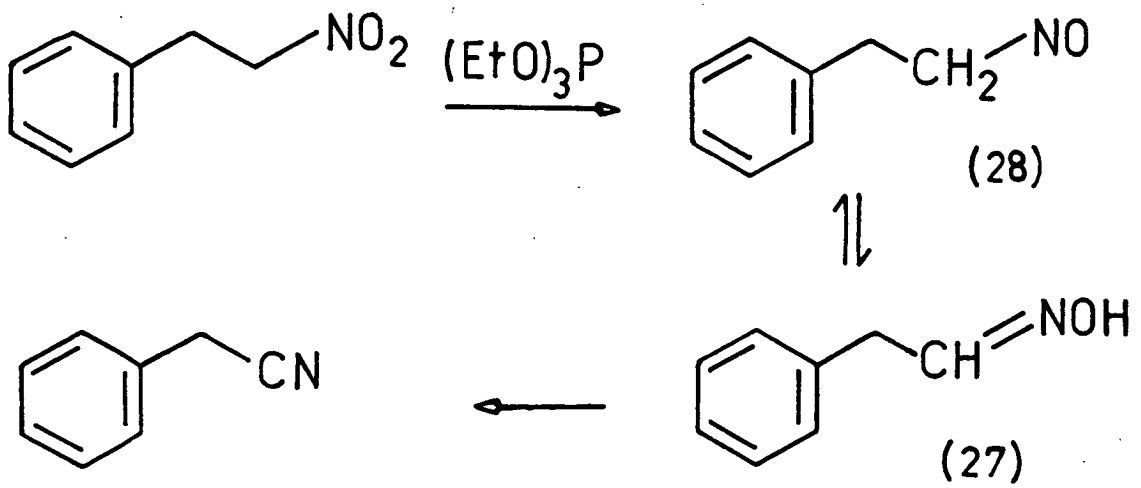
The rate of deoxygenation increases with increasing nucleophilicity of the phosphorus reagent. The results suggest the rate determining step involves nucleophilic attack by phosphorus on the nitro group.[17,60] The point of attack on the nitro group could be either at the nitrogen or the oxygen atom[2] (Scheme 23).

It is generally assumed that nitro deoxygenations proceed via the corresponding nitroso compound, but since the nitroso compound deoxygenates so much faster than the nitro compound, none has ever been



Scheme 23

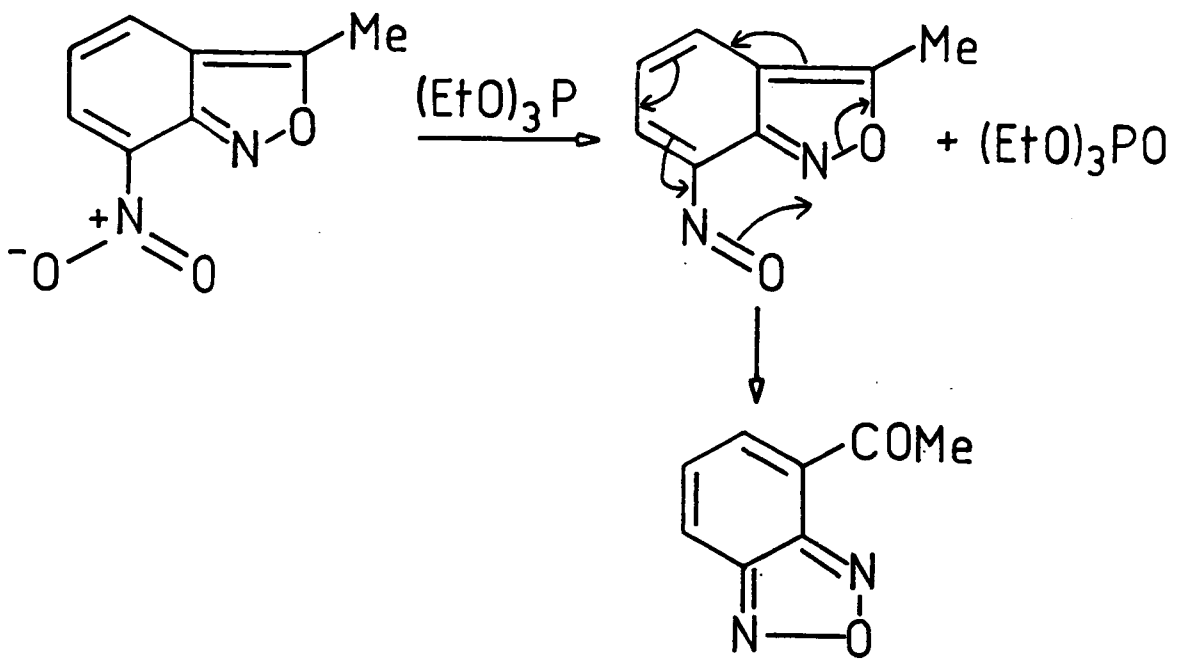
isolated from such a reaction and the evidence for their intermediacy is strictly limited. Reduction of 1-nitro-2-phenylethane with triethyl phosphite resulted in formation of phenylacetonitrile, which was assumed to occur via the oxime (27) since the oxime could also be deoxygenated to the nitrile[61] (Scheme 24). This could also provide evidence for a nitroso



Scheme 24

intermediate (28), although the oxime could be formed directly from deoxygenation of the aci-form of the nitro group. Katritzky[62] has shown that deoxygenation of 3-methyl-7-nitroanthranil by triethyl phosphite gives a 60% yield of 4-acetylbenzofurazan, which he suggests arises via the

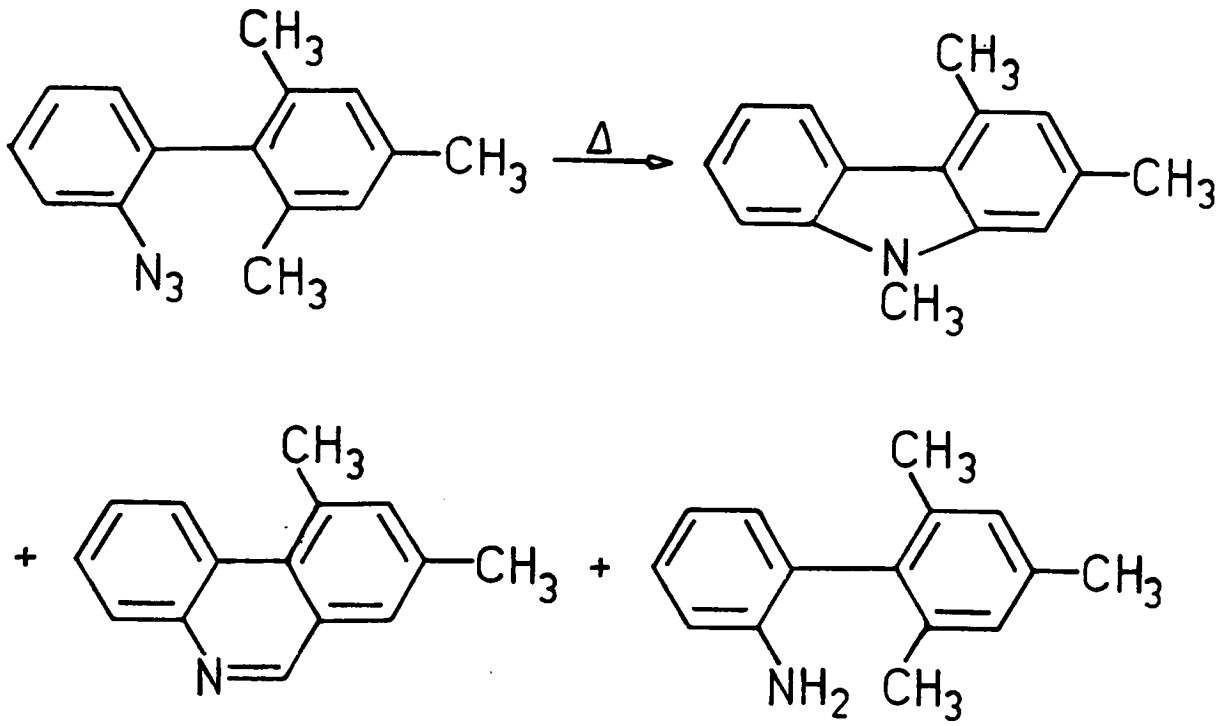
nitroso compound (Scheme 25), but the possible involvement of a precursor cannot be excluded.




Scheme 25

There is a much greater body of evidence for the intermediacy, or otherwise, of a discrete nitrene in the deoxygenation reactions. Abstraction and insertion reactions with C-H bonds are indicative of nitrenes.[42a] As has already been briefly commented on,[59] comparison of deoxygenation reactions with the corresponding azide thermolyses has often been used as a test for nitrenes.

Thermal decomposition of 2'-azido-2,4,6-trimethylbiphenyl in hexadecane at 230°C gave the nitrene-derived products, 2,4,9-trimethylcarbazole (4.5%), 8,10-dimethylphenanthridine (48%) and 2'-amino-2,4,6-trimethylbiphenyl (29%)[63] (Scheme 26). The deoxygenation of the corresponding 2',4',6'-trimethyl-2-nitrobiphenyl by triethyl phosphite has been investigated under a variety of conditions.[60] With a slight excess of triethyl phosphite, 2'-amino-2,4,6-trimethylbiphenyl and triethyl N-(2',4',6'-trimethylbiphenyl-2-yl)phosphorimidate were obtained, both



Scheme 26

indicative of a nitrene. The non-detection of the carbazole and the phenanthridine was attributed to more favourable combination of the nitrene with the excess phosphite. Supporting this conclusion was the observation that in solvent cumene or t-butylbenzene, the insertion product 8, 10-dimethylphenanthridine was formed. Additionally, in cumene there was formation of bi-$\alpha$-cumyl. This must arise by dimerisation of $\alpha$-cumyl radicals produced by abstraction of a hydrogen atom from cumene by a radical species, presumably the triplet nitrene (Scheme 27).

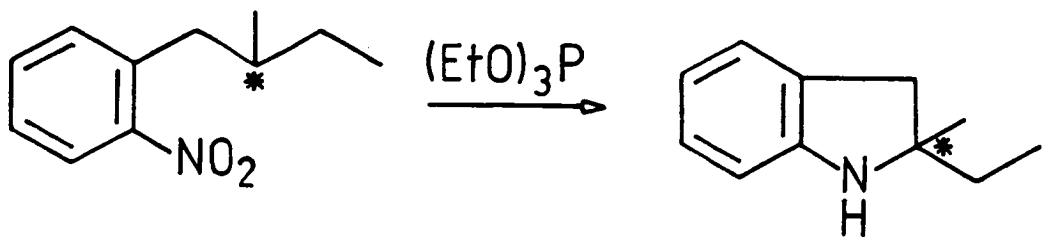
$$ArN\cdot + PhCHMe_2 \longrightarrow ArNH_2 + PhC\dot{M}e_2 \longrightarrow (PhCMe_2)_2$$

Scheme 27

2-Nitrobiaryls and 2-o-nitrophenylpyridine have also been found to behave similarly to the corresponding azides.[17]

Smolinsky[61] has shown that deoxygenation of (S)-(+)-2-nitro-1-(2-

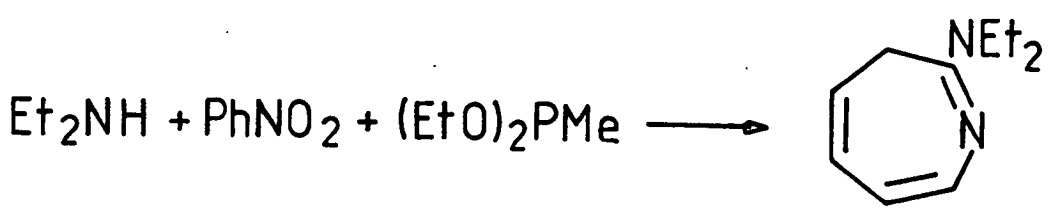
methylbutyl)benzene with triethyl phosphite gives a 25% yield of partially active indoline (Scheme 28). A comparable result was obtained with the




Scheme 28

corresponding azide thermolysis, again indicating a nitrene intermediate. It has similarly been found that triethyl phosphite deoxygenation of o-methyl-, o-propyl-, o-butyl-, o-cyclohexyl-,[64] and o-ethyl-[37] nitrobenzene gives mainly the triethyl N-arylphosphorimidates, but also significant amounts of amines (anilines, indolines, etc.) ascribed to abstraction and insertion reactions of nitrenes.

There is evidence of a similar nature to that already described[54] that 7-azabicyclo[4,1,0]hepta-2,4,6-triene may be an intermediate in the deoxygenation of nitrobenzenes. Reaction of nitrobenzene with diethyl methylphosphonite in a large excess of diethylamine gave 2-diethylamino-3H-azepine in 83% yield[60] (Scheme 29). The corresponding reaction of




Scheme 29

2-nitrobiphenyl gave 2-diethylamino-3H-3-phenylazepine (13%) in addition

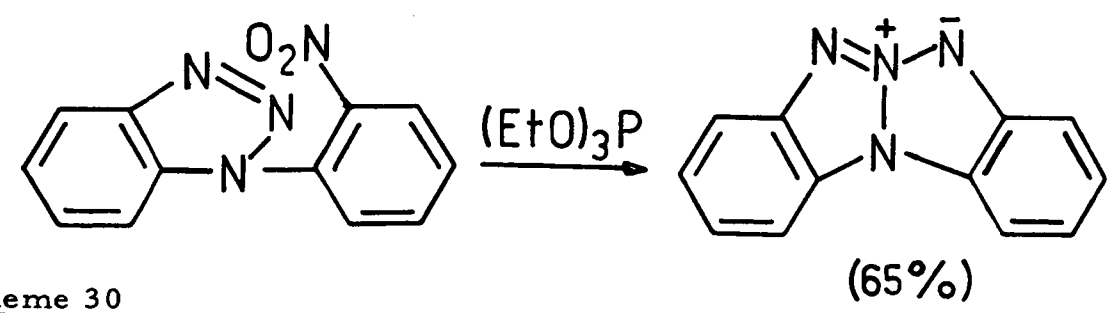
to carbazole (67%). This result suggests that either both products arise from the same intermediate, or that the nitrene and azabicycloheptatriene are in equilibrium.

In some cases where there are different patterns of product formation from the nitro and azido compound, this is taken as evidence for the participation of a nitrene precursor rather than a discrete nitrene in the deoxygenation reaction. Such a case is the deoxygenation of some aryl 2-nitrophenyl sulphides[65] (see next section).

(d) Use in Heterocyclic Ring Synthesis

From the point of view of using the deoxygenation reaction synthetically, the reduction of nitro compounds is much more useful than that of nitroso compounds simply because systems containing a nitro group are much more readily accessible than those with a nitroso group.

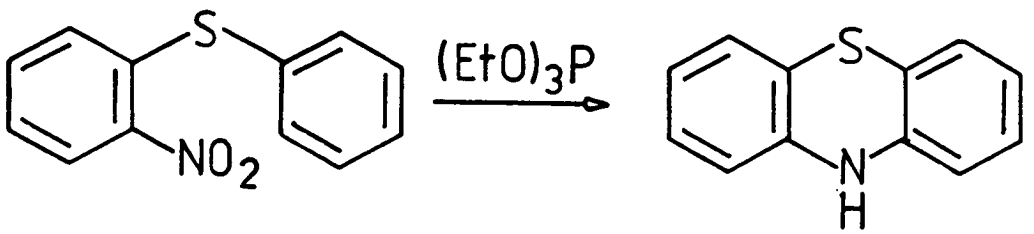
Nitrenes almost invariably react to give a five-membered ring in preference to a six-membered ring,[5] and for this reason a large number of five-membered ring systems have been synthesised via the deoxygenation reaction. Formation of carbazoles[17,36] from nitrobiphenyls has already been discussed, and some recent examples of this reaction have been reported.[66,67] Other systems which have been synthesised include indoles,[17,36,37] indazoles,[17,50] benzotriazoles,[17,50] benzimidazoles,[51] anthranils,[51] and more complex systems such as tetraazapentalenes[17,68] (e. g. Scheme 30). These reactions in general make use of a nitro compound




Scheme 30

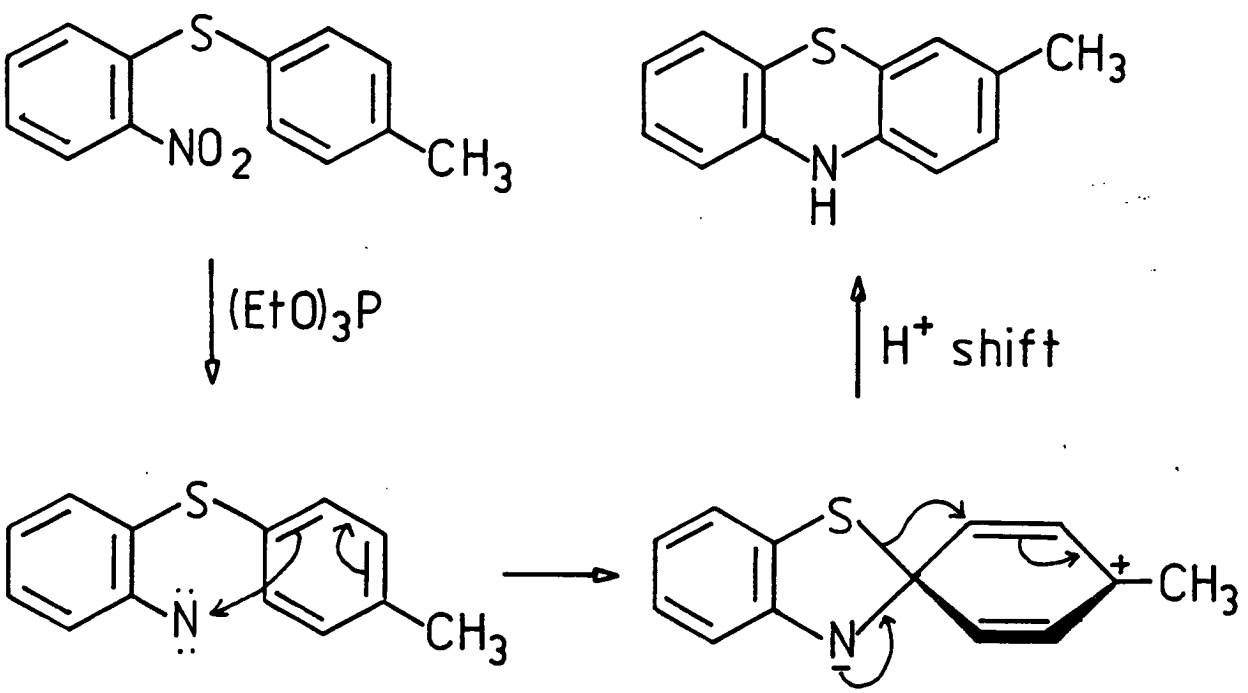
with a suitable o-side chain.

A number of examples of six-membered ring systems have also been synthesised. Cadogan and co-workers[69] found that deoxygenation of phenyl 2-nitrophenyl sulphide with triethyl phosphite gave phenothiazine in 54% yield (Scheme 31). This appears to be simply direct nitrene insertion at a position ortho to the sulphur atom; however, deoxygenation




Scheme 31

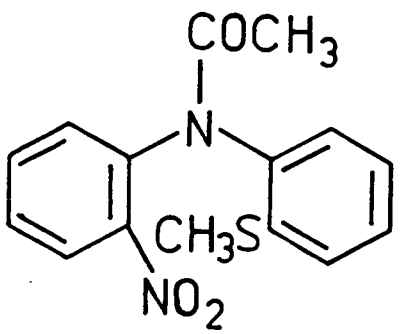
of 4-methylphenyl 2-nitrophenyl sulphide gave the unexpected 3-methyl-phenothiazine (56%). This result was explained by a rearrangement mechanism involving a spiro-diene intermediate (Scheme 32). Therefore,




Scheme 32

even in this case, reaction proceeds via initial formation of a five-membered ring. The reaction can be extended to give interesting nitrene-induced rearrangements by blocking the ortho positions in the aryl ring.[65]

A similar rearrangement to that above occurs in the formation of dihydrophenazines from N-acetyl-2-nitro-2'-methylthiodiphenylamine (29).[70]




(29)

Phenazines themselves have been shown to be formed by triphenylphosphine deoxygenation of $Cu^{II}$ and $Fe^{III}$ complexes of 2-nitrosophenols.[71]

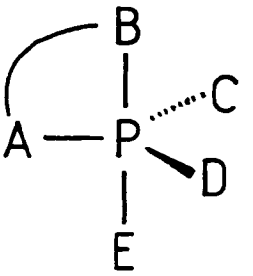
Synthesis of quinolines[44,45] has already been discussed in section A. 3(a).

Seven-membered ring formation is less common, but one can cite the formation of 3H-azepines[54,60] when the deoxygenation reaction is carried out in the presence of amines.

## B. Penta-coordinate Phosph(v)oles

### B. 1 General

Penta-coordinate phosph(v)oles are compounds with the general structure (30) where the phosphorus is contained in a five-membered ring and is bonded to five other atoms, usually in a trigonal bipyramidal




(30)

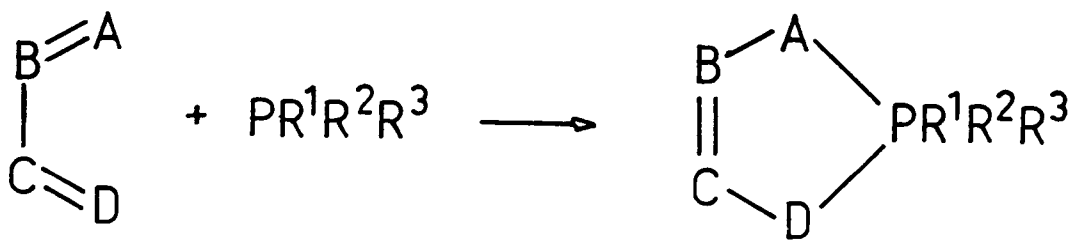
configuration. The general term 'phosphorane' is often used in connection with these cyclic phosph(v)oles, although the term strictly applies to all P(V) species. A general feature of these penta-coordinate phosphorus species[72] is that they all exhibit a negative chemical shift in the $^{31}P$ n. m. r. spectrum, relative to 85% external phosphoric acid taken as zero p. p. m. Shifts ($\delta$) to high frequency of the standard are positive.

An enormous number of phosph(v)oles have been synthesised, but only in a few cases has their chemistry been studied in depth. Many of the reactions employed exhibit certain common features and because of this, a certain amount of order can be brought to bear on this huge field. The following sections will attempt to classify some of these phosphoranes in a reasonably logical manner. The first section will deal with those phosph(v)oles which can be considered to arise formally by Michael addition of a tervalent phosphorus reagent to an $\alpha,\beta$-unsaturated system. The second section will consider miscellaneous other phosph(v)oles, some of

which are related to each other and/or to those discussed in section B. 2.

B. 2 Phosph(v)oles Formed Formally by Michael Addition to α, β-Unsaturated Systems.

These are formed by the general reaction shown below (Scheme 33). This is such a large field that this section is further sub-divided into

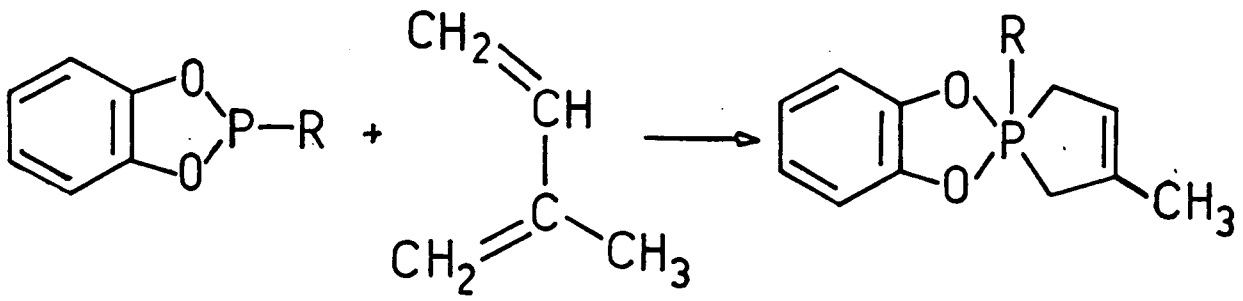



Scheme 33

sections considering phosph(v)oles arising from the same type of α, β-unsaturated system.

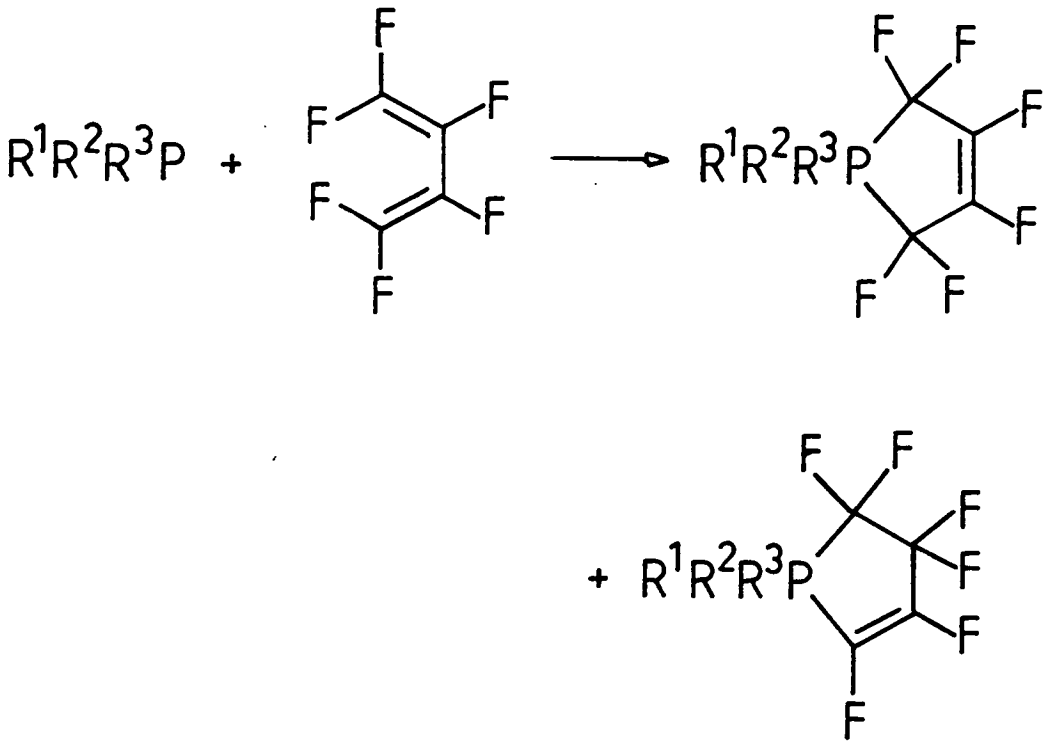
(a) Phosph(v)oles from 1, 3-Dienes

Isoprene reacts with 2-substituted 1, 3, 2-benzodioxaphospholans to give the phosph(v)ole in high yield[73] (Scheme 34). A similar reaction has been found with hexafluorobutadiene, which reacts with a variety of




R = $CH_3$ , Ph

Scheme 34

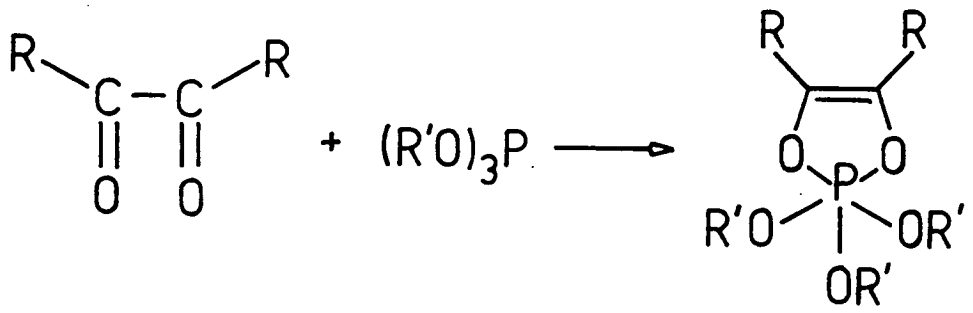


Scheme 35

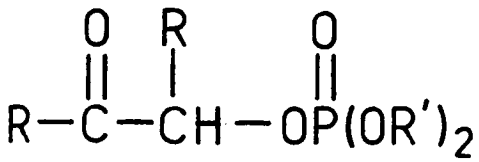
trivalent phosphorus compounds at low temperature to give a mixture of phosphoranes[74] (Scheme 35). These often decompose to give difluoro-phosphoranes $R^1R^2R^3PF_2$ on standing.

(b) Phosph(v)oles from 1,2-Dicarbonyl Compounds

This is a reaction which has been known for many years. Kukhtin[75] first suggested the possibility of a cyclic phosphorane intermediate in the reaction of biacetyl with trialkyl phosphites, and proceeded to show that these could be isolated under mild conditions. Analogous reaction of trialkyl and triaryl phosphites with o-quinones and α-diketones led to the formation of crystalline adducts in nearly quantitative yield[76] (Scheme 36). These adducts were stable in the absence of air and moisture. The trimethyl phosphite adducts reacted with anhydrous hydrogen chloride to give α-keto monophosphates (31). Reactions with bromine were also



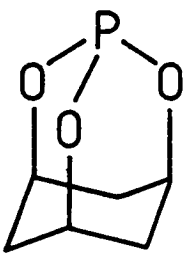
Scheme 36



(31)

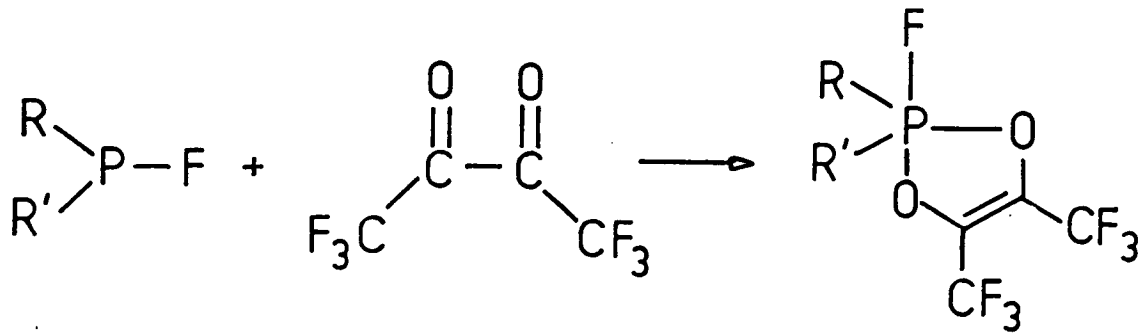
reported. Full spectral data (I. R., Raman, $^{31}$P n. m. r., $^{1}$H n. m. r.) for these adducts have also been published.[77]

The very reactive hexafluorobiacetyl reacted very rapidly with trimethyl phosphite and 1-phospha-2, 8, 9-trioxaadamantane (32) to give a



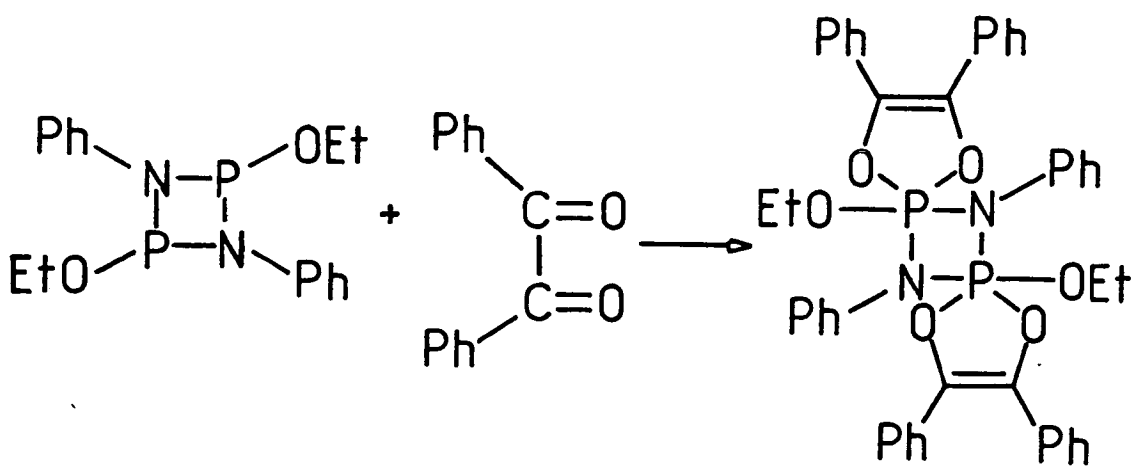
(32)

monocyclic and a caged polycyclic pentaoxyphosphorane respectively.[78] Oxidative addition of fluorophosphines and fluorophosphites to hexafluorobiacetyl also resulted in the formation of stable cyclic oxyphosphoranes[79] (Scheme 37). The temperature dependence of the $^{19}$F n. m. r. spectra was discussed in terms of pseudorotation at phosphorus (V). All these phosphoranes contain the 1, 3, 2-dioxaphospholene ring system. Adducts



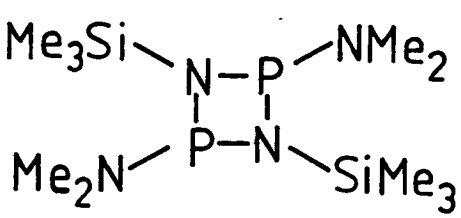
Scheme 37

where the phosphorus is also part of a diazadiphosphetidine ring have been synthesised in the same way. Examples of such reactions are the addition of 2,4-diethoxy-1,3-diphenyl-1,3,2,4-diazadiphosphetidine to benzil[80] (Scheme 38), and the low temperature reaction of biacetyl with



Scheme 38

the silyl compound (33).[81]

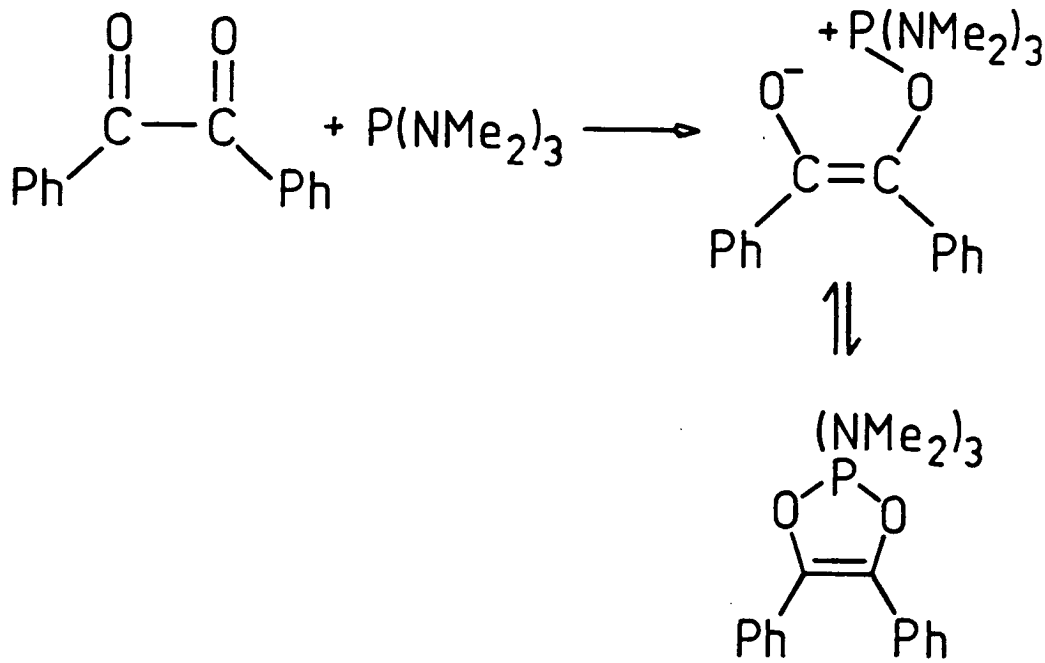


(33)

The corresponding sulphur analogues, the oxathiaphospholenes,

have been prepared by reaction of monothiobenzil with trimethyl phosphite and dimethyl phenylphosphonite.[82]

When tris(dimethylamino)phosphine was reacted with benzil, the resultant 1:1 adduct could be isolated in two crystalline forms, one a dipolar ion and the other a cyclic phosphorane[83] (Scheme 39).

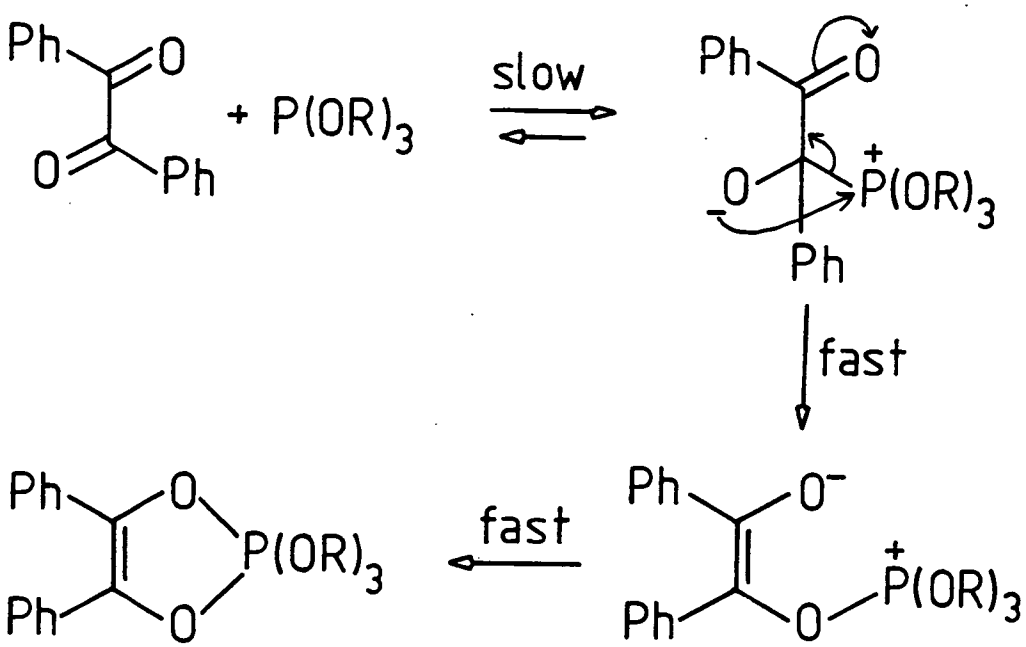


Scheme 39

Solutions of these contained the same molecular species in equilibrium, the equilibrium being solvent dependent. The cyclic phosphorane structure is increasingly favoured over the corresponding open-chain dipolar structure in the series 1, 2, 3-triketones < o-quinones < *a*-diketones, as a result of decreasing charge delocalisation in the series. There is a greater tendency to form the pentavalent phosphorus compound with phosphites and with the five-membered cyclic tris(dialkylamino)phosphines than with acyclic tris(dialkylamino)phosphines.

There has been some debate about the mechanism of formation of these phosph(v)oles. Studies of the kinetics of the reaction of benzil with trialkyl phosphites supported a mechanism proceeding by nucleophilic

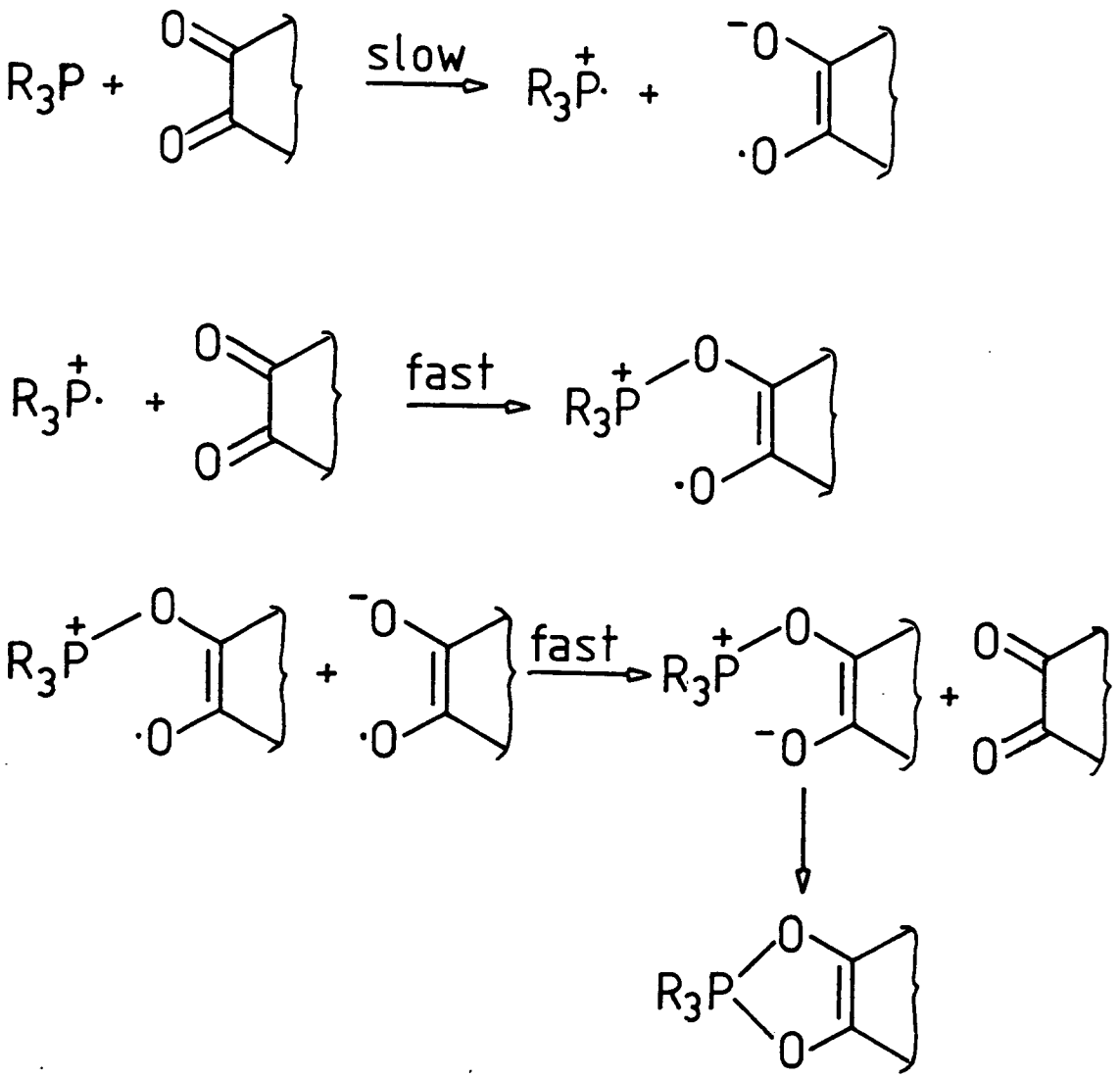
attack of the phosphorus atom on the carbonyl carbon[84, 85] (Scheme 40).



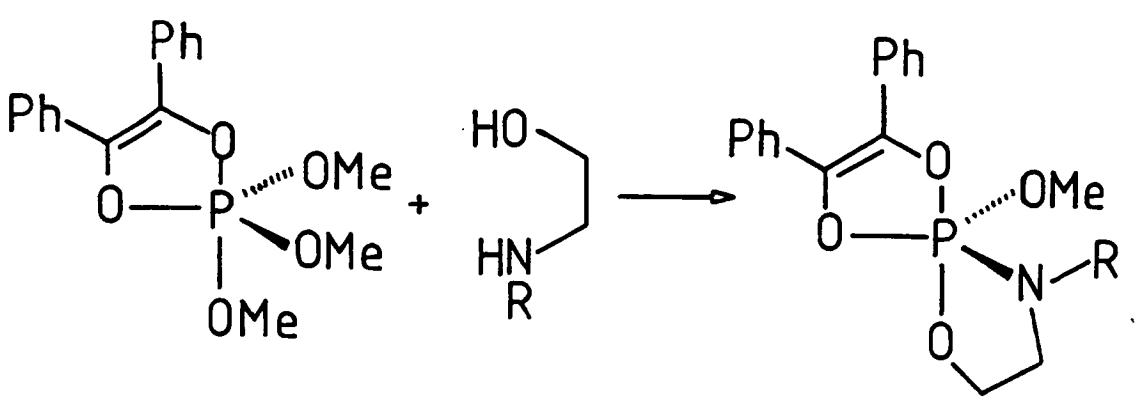

Scheme 40

The results excluded a concerted cycloaddition reaction, which would require attack on oxygen. There is, on the other hand, convincing e. s. r. evidence that radical intermediates are involved in the reaction of tervalent phosphorus compounds with activated carbonyl compounds such as α-diketones, o-quinones, and α,β-unsaturated ketones.[86] (Scheme 41). The first formed phosphinium radical reacts rapidly with a carbonyl function.

A large number of reactions of the oxyphosphoranes have been reported, and their application in synthesis has been reviewed.[87] Ligand exchange reactions of the pentaoxyphosphoranes with aminoalcohols or diols provides a route to spirophosphoranes[88] (Scheme 42).



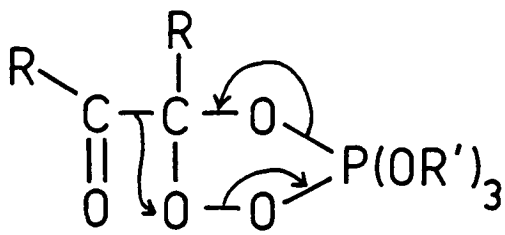
Scheme 41



Scheme 42

The adducts react with molecular oxygen, leading to a carbon

skeleton rearrangement.[89] For example, reaction of the benzil-trimethyl phosphite adduct with dry oxygen gave benzoic anhydride (30%), benzil (67%) and trimethyl phosphate (94%). It has been suggested that the rearrangement involves an intermediate (34) similar to an ozonide. This could decompose to the anhydride or react with more adduct to give

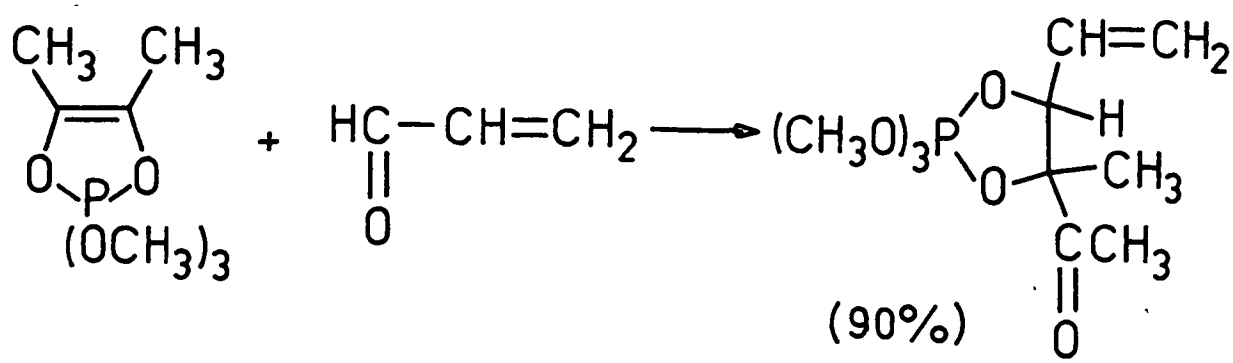


(34)

the original α-diketone.

The oxyphosphoranes derived from o-chloranil and hexafluorobiacetyl have been used as models in connection with the conversion of ATP into cyclic-AMP.[90]

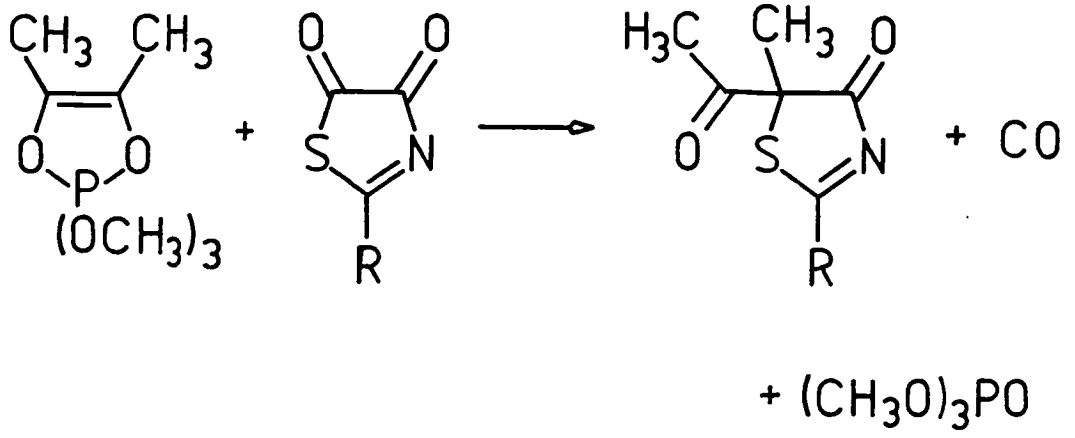
The phosphoranes in general react with carbonyl compounds, such as acrolein, in a nucleophilic 1, 2-addition to the carbonyl function, a reaction which Ramirez[91] has termed the "oxyphosphorane condensation" (Scheme 43). With 2-thiazolin-4, 5-diones, the biacetyl-trimethyl phosphite



(90%)

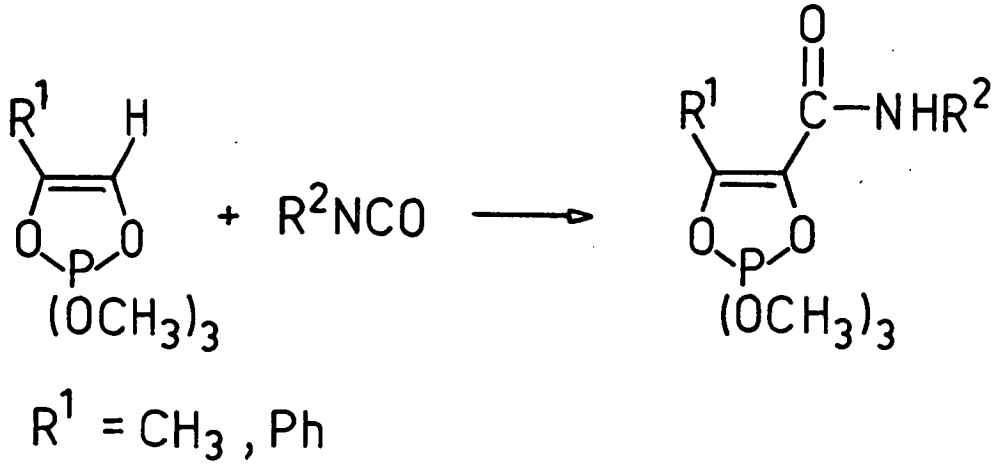
Scheme 43

adduct reacted to give the corresponding 5-acetyl-5-methyl-2-thiazolin-4-one with loss of trimethyl phosphate and carbon monoxide[92] (Scheme 44).



Scheme 44

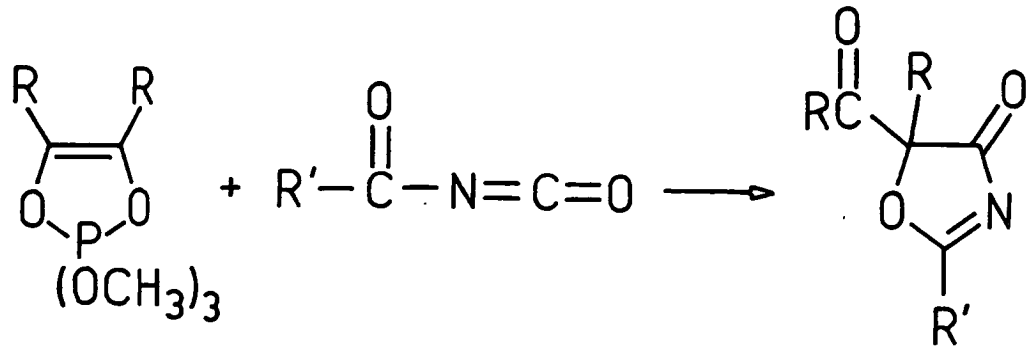
The phosphoranes also react with heterocumulenes such as isocyanates.[93-96] The trimethyl phosphite adducts of pyruvaldehyde and phenylglyoxal reacted with isocyanates to form the carbamyl-1, 3, 2-dioxaphospholenes[93] (Scheme 45). Reaction of the pentaoxyphosphoranes



Scheme 45

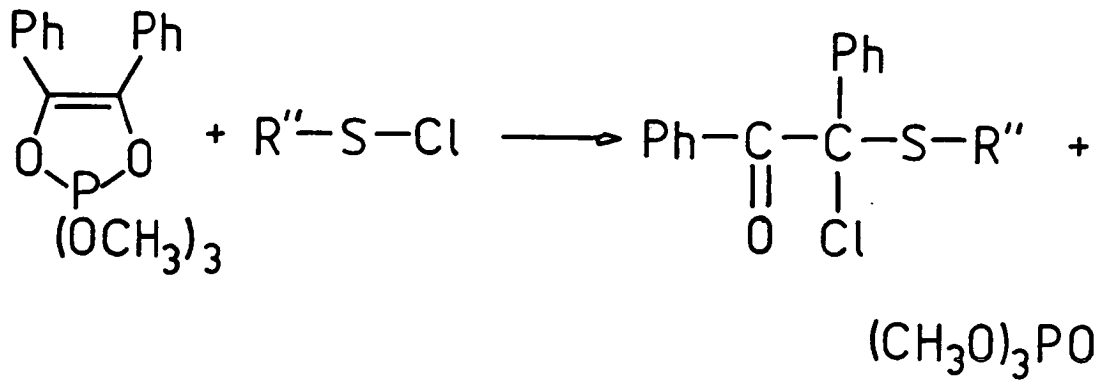
with acyl isocyanates leads to the formation of 2-oxazolin-4-ones[94, 95, 96] (Scheme 46).

Reaction of the benzil-trimethyl phosphite adduct with sulphenyl chlorides is rapid and results in the formation of high yields of α-chloro-β-keto sulphides (Scheme 47), useful intermediates in the synthesis of



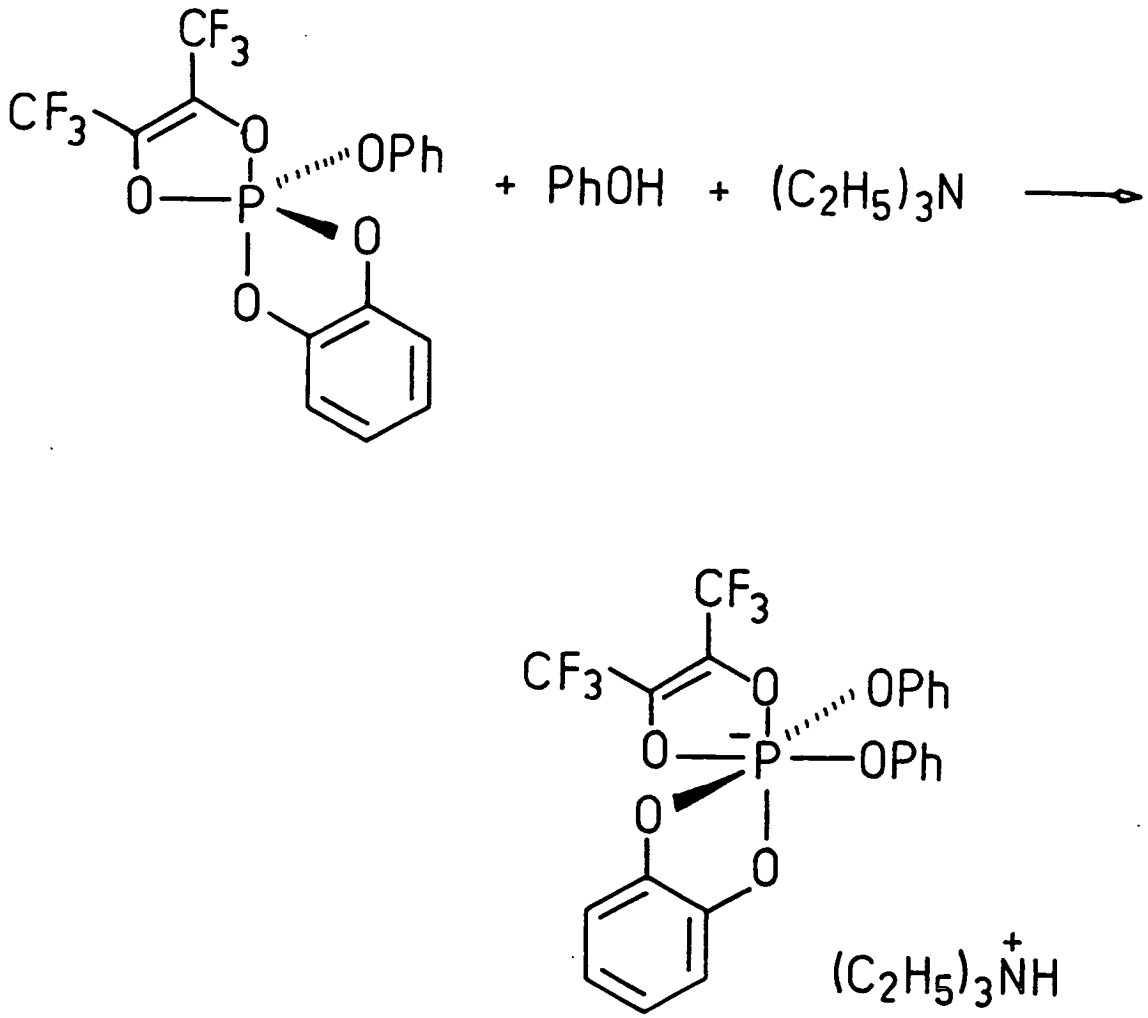
Scheme 46

α-hydroxy acids, α-keto aldehydes, etc.[97] Cyclopropanes can be formed



Scheme 47

by the reaction of the biacetyl-trimethyl phosphite adduct with arylidene malononitriles.[98] The diketone-phosphite adducts can be catalytically hydrogenated to give high yields of phosphate and monoketone.[99] Since diketones are available from simple monoketones, the reaction is a potential solution to the difficult synthetic problem of ketone transposition. Where both electronic and steric factors are operating, high selectivity can be shown towards a single product. Finally, crystalline six-coordinate phosphorus compounds have been formed from the spiropentaoxyphosphorane derived from hexafluorobiacetyl and phenyl o-phenylene phosphite.[100] Reaction with pyridine gives a zwitterion, whereas the use of phenol in the presence of triethylamine gives an ion-pair (Scheme 48).

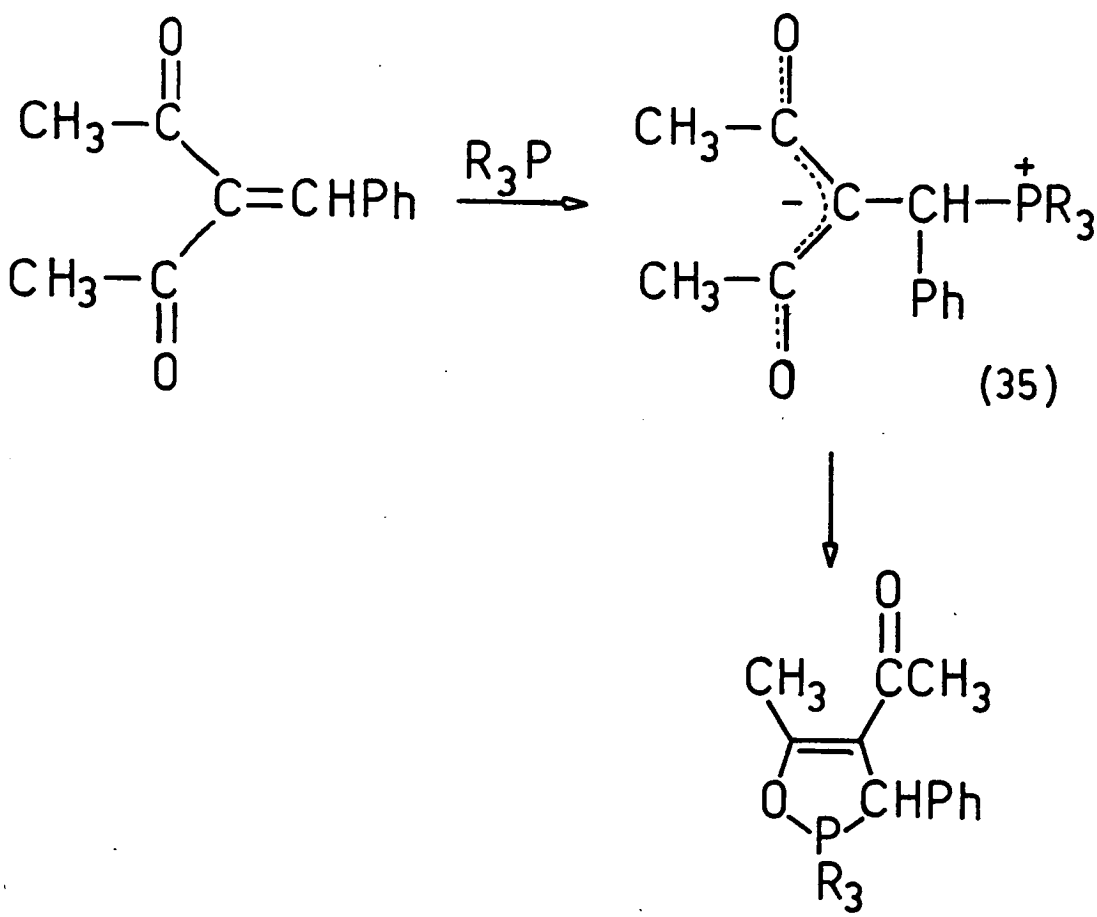



Scheme 48

(c) Phosph(v)oles from α,β-Unsaturated Carbonyl Compounds

The discussion in this section will be limited to those compounds where the unsaturation is due to a carbon-carbon double bond. Other types will be considered later.

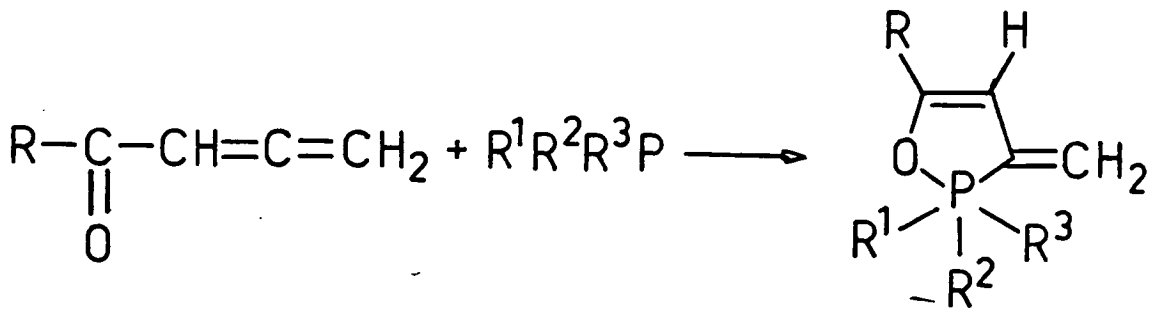
Reaction of 3-benzylidene-2,4-pentanedione with trimethyl phosphite has been found to give the phosphorane, presumably via a dipolar intermediate (35)[101] (Scheme 49). The phosphorane reacted with water to




Scheme 49

give an enol phosphonate which tautomerised to the β-diketone phosphonate. Phosphoranes were also obtained using phosphonites and phosphinites;[102] however, when trialkyl- and dialkylaryl-phosphines were used, the adducts obtained appeared to be the open dipolar ions (35) on the basis of the spectral data.[103] From these observations, it appears that at least one oxygen

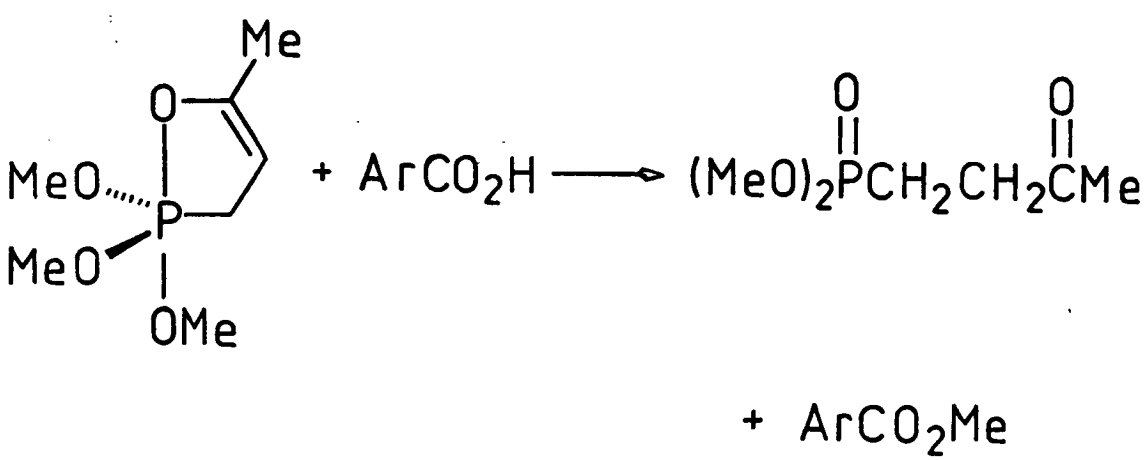
atom must be attached to the phosphorus in the tervalent phosphorus reagent for cyclisation to occur. α-Allenic ketones reacted quantitatively with phosphites, phosphonites, and phosphinites to give an oxaphosphole with an exocyclic double bond[104] (Scheme 50).



Scheme 50

A study[105] of the condensation of methyl vinyl ketone with phosphonites derived from pyrocatechol showed that the Hammett $\rho$ values were negative, a result which is consistent with the phosphorus atom acting as a nucleophile.

It has been found that these oxaphospholenes are powerful O-alkylating agents.[106] For example, mesitoic acid, which normally requires harsh reaction conditions, can be esterified smoothly at room temperature (Scheme 51). Phenols can also be alkylated. The O-alkylation reaction has been

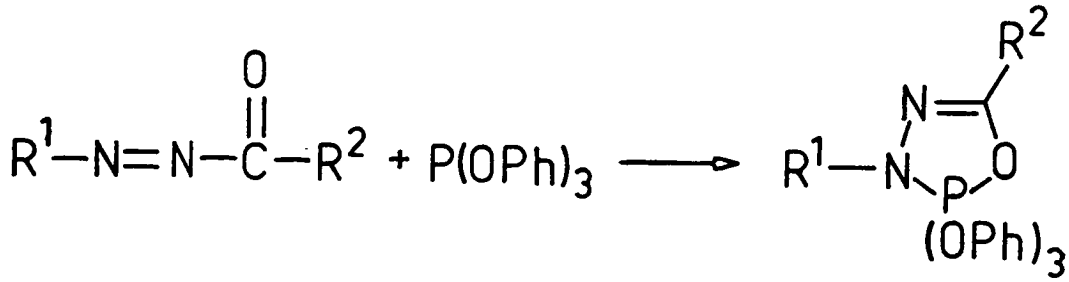


Scheme 51

used as a model system for biochemical conversions.[107]

(d) Phosph(v)oles from Azo Compounds

Phosph(v)oles have been prepared from azocarbonyl compounds by reaction with triphenyl phosphite[108] (Scheme 52), and a similar reaction occurs with trimethyl phosphite.[109] These phosphoranes are hydrolysed

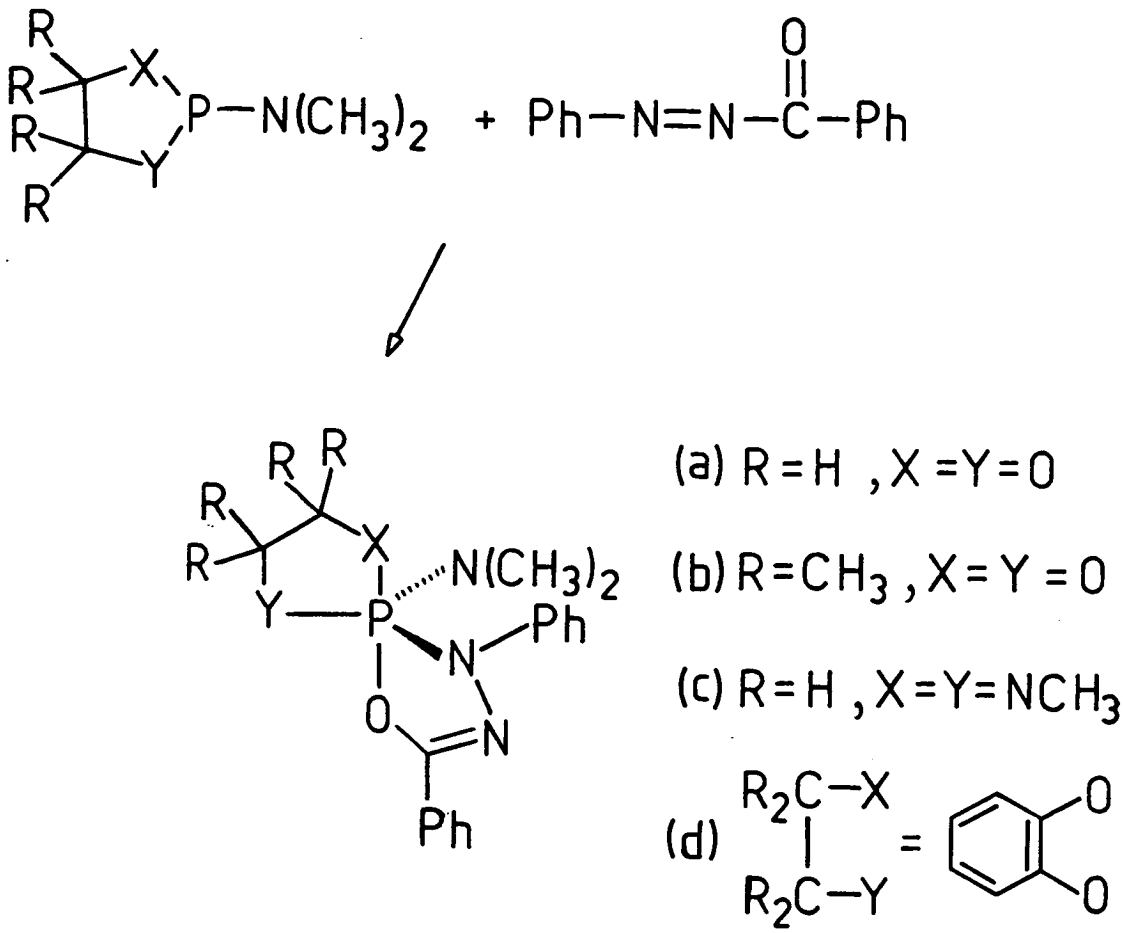


(a) $R^1 = R^2 = Ph$

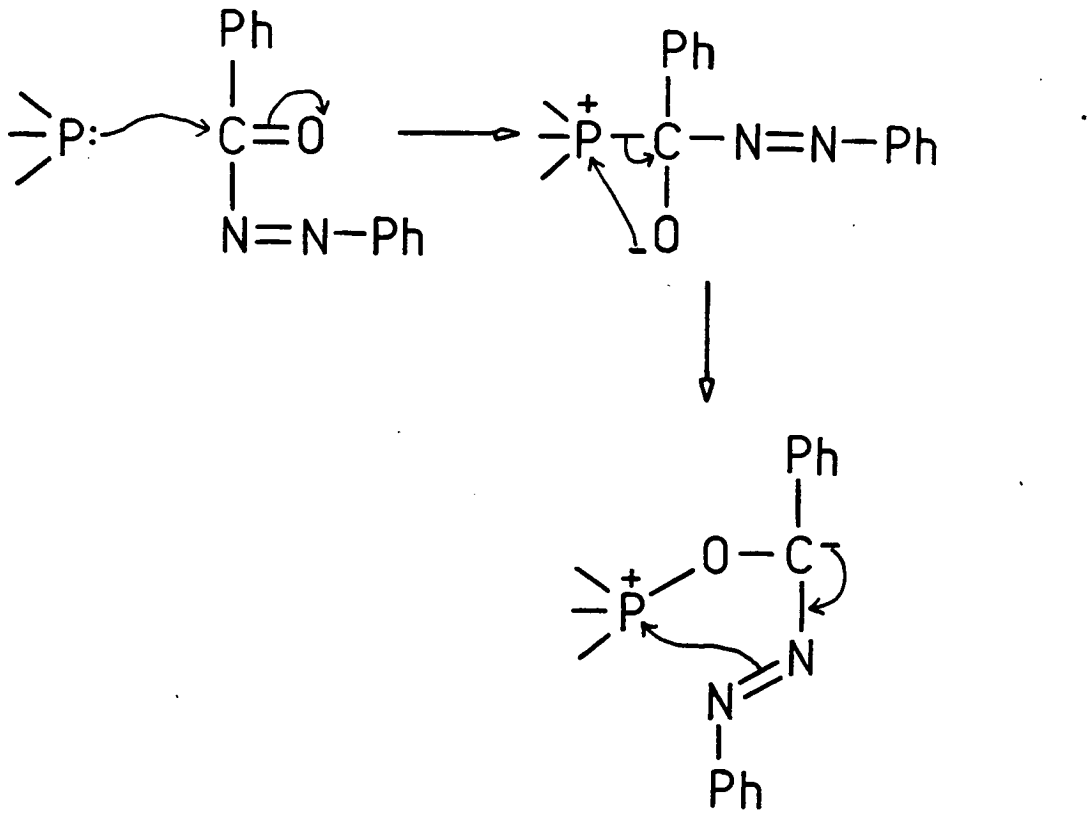
(b) $R^1 = CO_2Me$ , $R^2 = OMe$

Scheme 52

to triphenyl phosphate and the corresponding hydrazo compound. Reaction of N-phenyl-N'-benzoyldiimide with trimethyl phosphite gave an oily cyclic tetraoxyphosphorane, whereas the phosphorane obtained from 1-phospha-2, 8, 9-trioxaadamantane was a crystalline solid.[110] An X-ray crystallographic study confirmed the phosphorane structure and showed a distorted trigonal bipyramid with a five-membered ring in an apico-equatorial skeletal position with the oxygen apical and the nitrogen equatorial. Certain amino-phosphorus compounds also reacted with N-phenyl-N'-benzoyldiimide to give spirophosphoranes[111] (Scheme 53). A mechanism has been proposed, involving a zwitterionic addition intermediate which then cyclises (Scheme 54). There is the additional possibility of Michael attack at the nitrogen β to the carbonyl group, either by a concerted or stepwise mechanism.

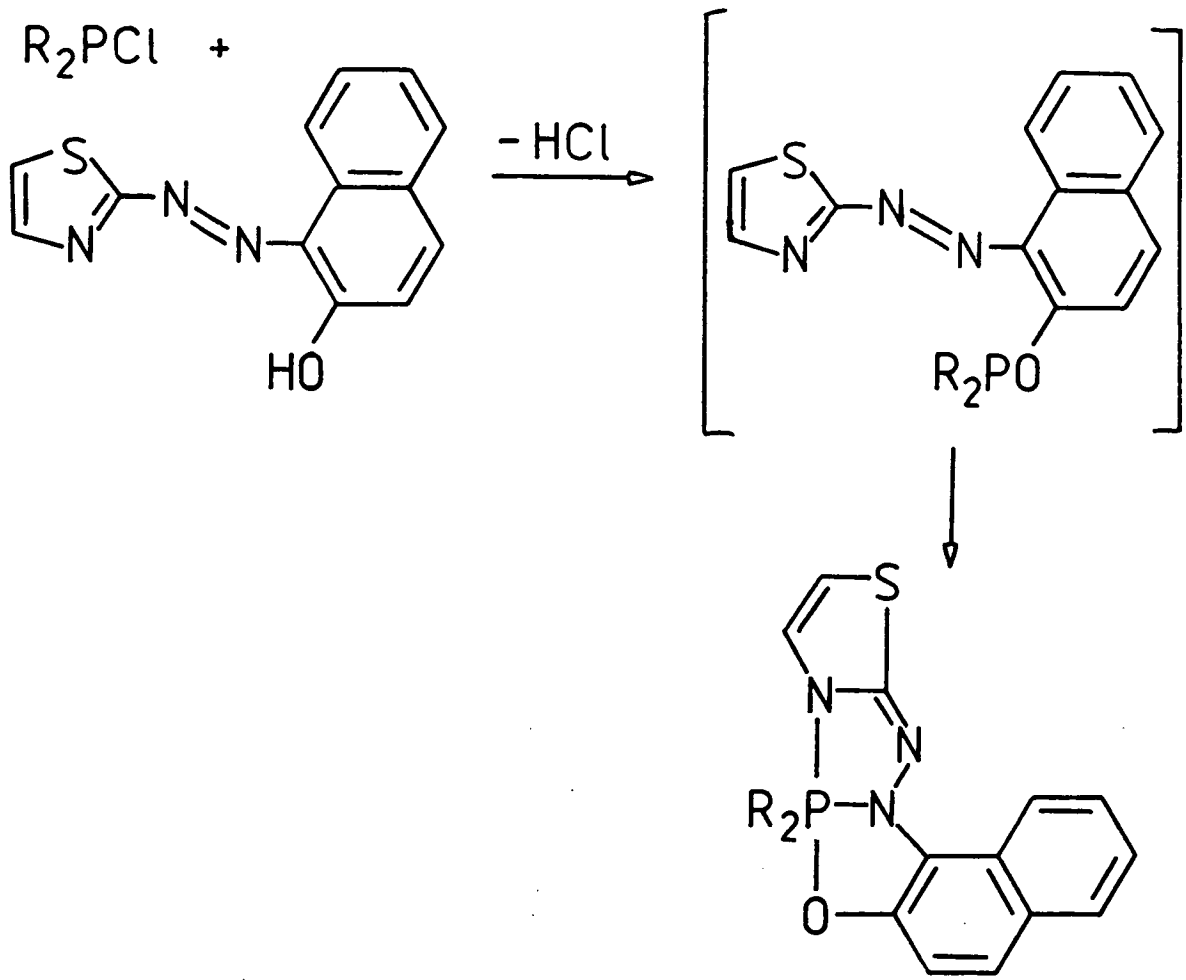



Scheme 53




Scheme 54

Related reactions occur by treating 1-(2-pyridylazo)- and 1-(thiazol-2-ylazo)-2-naphthol with chlorophosphines[112] (Scheme 55). In this case,



Scheme 55

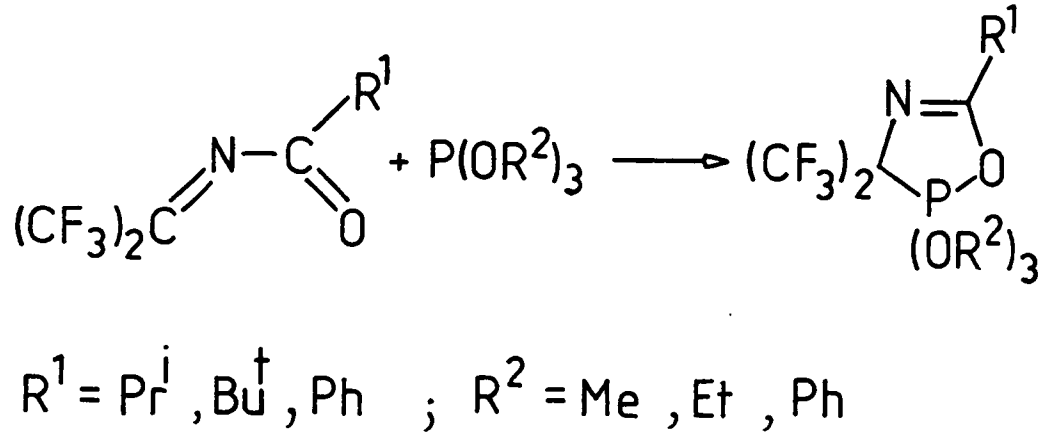
the reaction proceeds *via* substitution intermediates which then undergo a [4+1] cycloaddition reaction.

The intermediacy of a phosphorane has been postulated in the reaction of azoalkenes with trimethyl phosphite.[113]



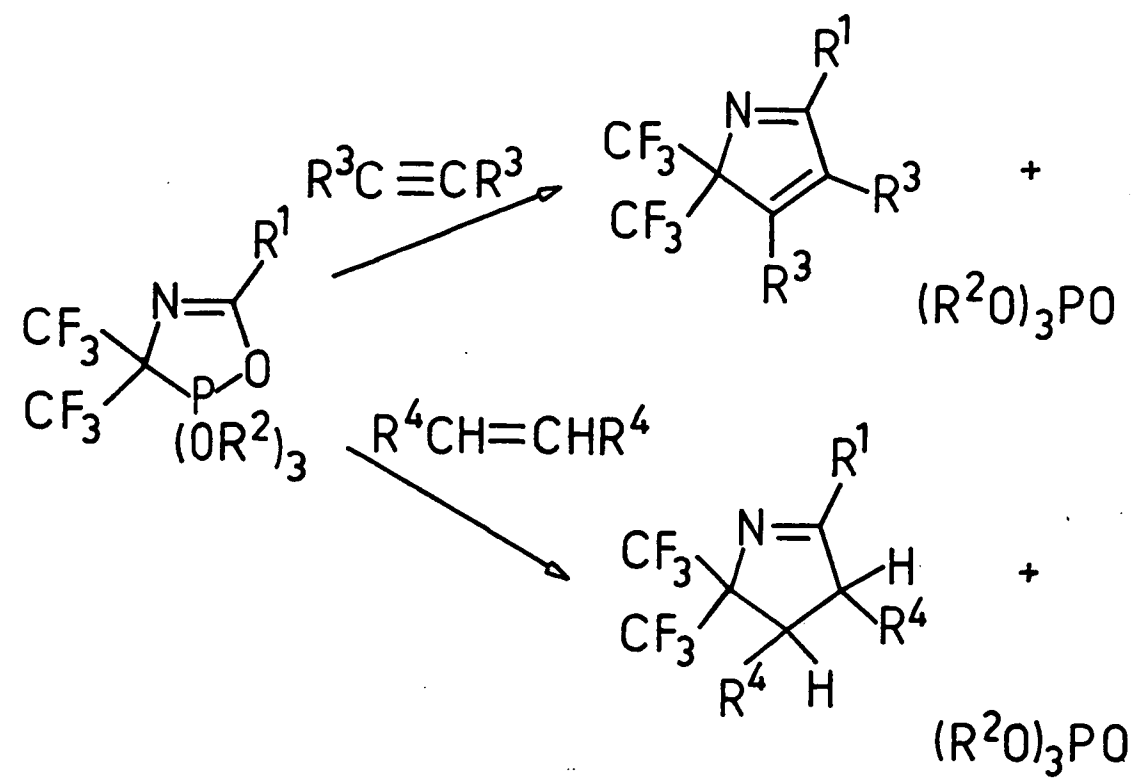
(e) Phosph(v)oles Derived from other Conjugated Systems

Burger[114] has shown that 1, 1, 1, 3, 3, 3-hexafluoro-2-(acylimino)-propanes undergo a [4+1] cycloaddition reaction with trialkyl and triaryl phosphites to give 4, 5-dihydro-1, 3, 5-oxazaphosph(v)oles in high yield (Scheme 56). These all exhibit characteristic $^{31}P$ n.m.r. shifts between

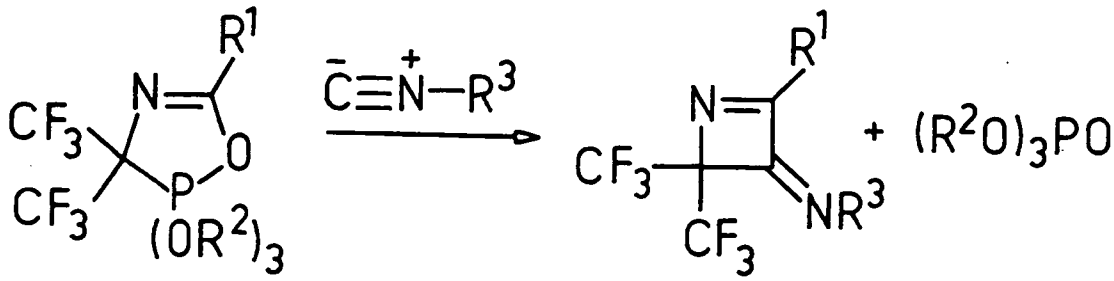


Scheme 56

-30 and -40 p. p. m. These phosph(v)oles cleave out nitrile ylides via a cycloelimination reaction on thermolysis[115] and photolysis.[116] The nitrile ylides can be trapped with alkynes and alkenes to give generally good yields of 2H-pyrroles and pyrrol-1-ines respectively (Scheme 57). The phosphoranes also react with isocyanides in boiling benzene in a [3+1] cycloaddition reaction to give good yields of azetines[117] (Scheme 58). The nitrile ylides have been trapped with other multiple bond systems



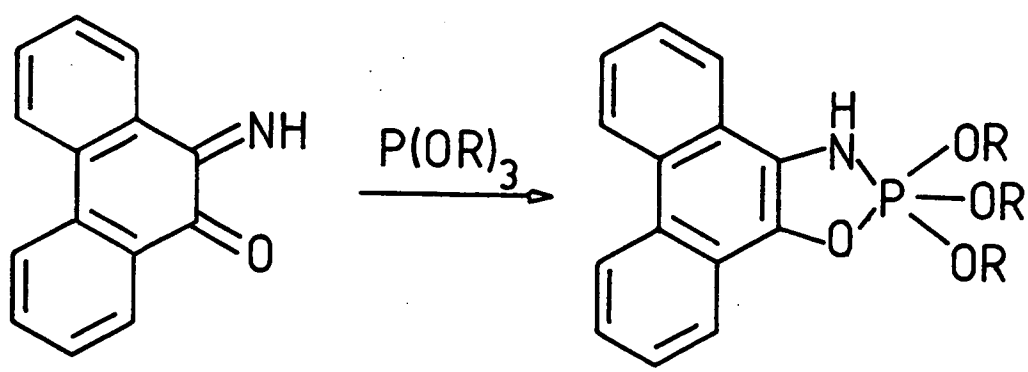
Scheme 57



Scheme 58

such as azo compounds,[118,119] benzonitrile,[118] and nitrosobenzene.[120] The regular permutational isomerizations of the oxazaphosph(v)oles have been investigated by n. m. r.[121]

α-Ketone imines also react with tervalent phosphorus reagents to give 1, 3, 2-oxazaphosph(v)oles.[122,123] Reaction of phenanthrenequinone-monoimine with trialkyl phosphites gives crystalline adducts (Scheme 59) which are moisture sensitive and stable for only a few days.[122] Oxidation

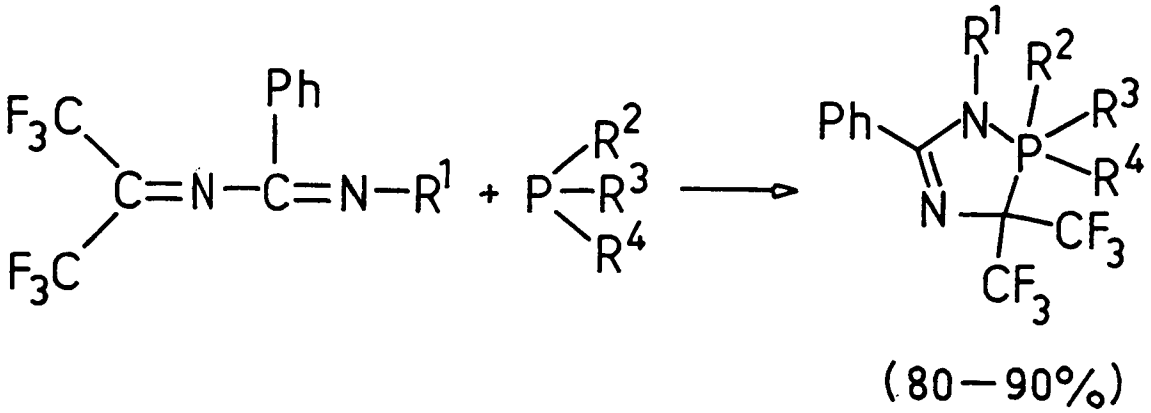


Scheme 59

of the phosphorane leads to phenanthrenequinone, and the same product is formed on treatment with 10% aqueous sodium hydroxide. It has been shown that the ketone imines are much less reactive than the corresponding α-diketones in their reaction with tervalent phosphorus reagents.[123] If the nucleophilic character of the phosphorus reagent is reduced, the rate

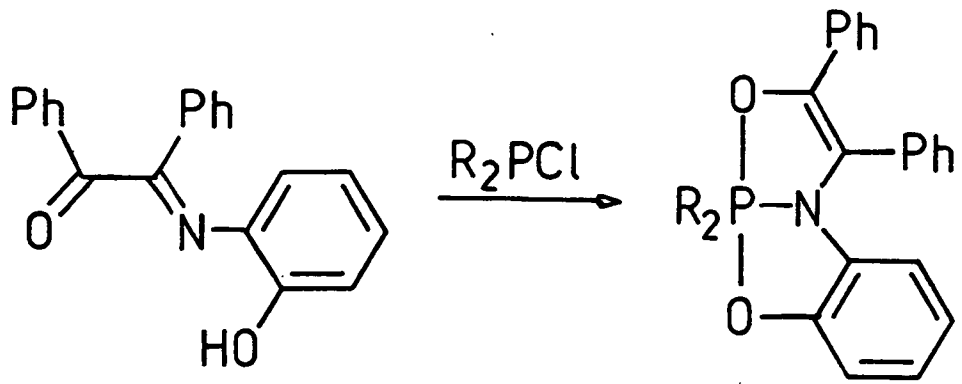
of reaction decreases.

2, 3-Dihydro-1, 4, 2-diazaphosph(v)oles are formed by reaction of N-(hexafluoro-2-propyliden)-N'-arylbenzamidines with trimethyl and triethyl phosphite, and with dimethyl phenylphosphonite at -20°C in hexane[124] (Scheme 60).




Scheme 60

Other examples of phosphoranes formed via initial substitution intermediates (cf. section B. 2(d)) have been reported. Acyclic and cyclic chlorophosphines reacted with benzil mono(o-hydroxyanil) to give bi- and tricyclic phosphoranes respectively[125, 126] (Scheme 61). A crystal




Scheme 61

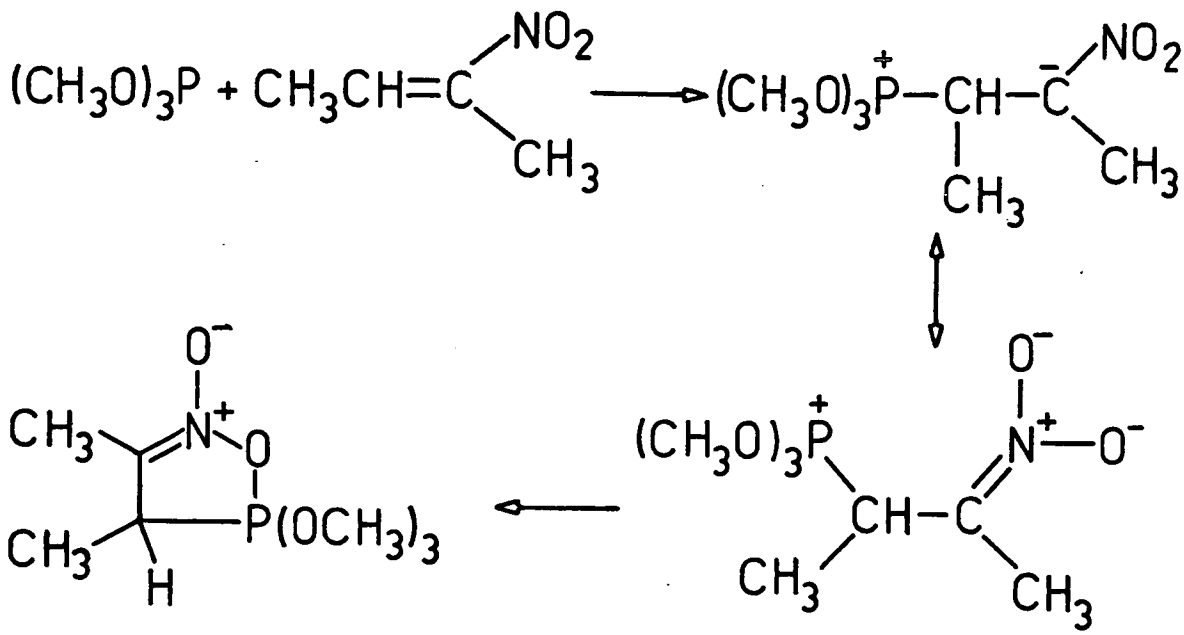
structure determination of the phosphorane derived from 2-chloro-1, 3, 2-dioxaphospholan has shown that the dioxaphospholan ring adopts an axial-

equatorial position.[127] An analogous reaction has been observed with N'-(2-pyridyl)benzil monohydrazone.[112]

(f) Phosph(v)oles Derived from Nitroalkenes

The reaction of nitroalkenes with tervalent phosphorus reagents is formally related to the reactions already described, as the nitro group can be considered to have a nitrogen-oxygen double bond. In a number of cases, the reaction has been found to lead to the formation of phosph(v)oles.

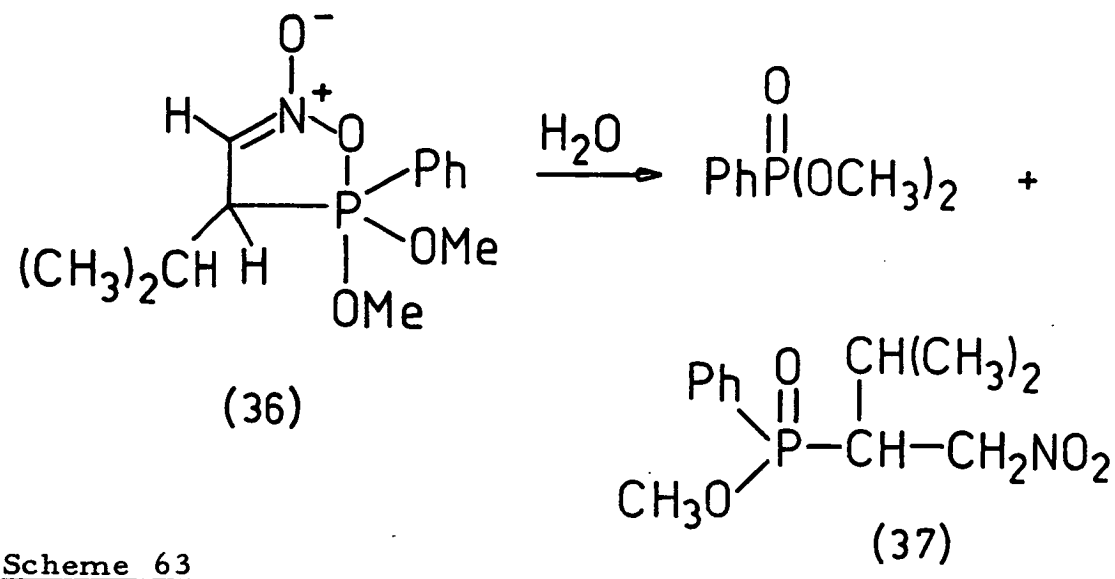
Gareev[128] has shown that reaction of 2-nitrobut-2-ene with trimethyl phosphite gives the solid 2-oxo-1, 2, 5-oxazaphosph(v)ole in 88% yield. He postulated initial attack of the phosphite on the activated double bond to give a 1, 3-dipolar ionic intermediate, which undergoes an electron shift to the 1, 5-dipolar ion which then cyclises to the product (Scheme 62).



Scheme 62

The $^{31}P$ n.m.r. shift is changed very little on changing from a solvent of low polarity (benzene) to one of high polarity (acetone), indicating the absence of an equilibrium between the cyclic form and the open-chain

dipolar form. A similar phosphorane was obtained from the reaction of 3-methyl-1-nitro-but-1-ene with dimethyl phenylphosphonite.[129] These phosphoranes are thermally unstable and also hydrolytically sensitive. For example, thermolysis of phosphorane (36) resulted in loss of methyl nitrite and formation of dimethyl phenylphosphonate and methyl (1-isopropylvinyl)phenylphosphinate, while reaction with water afforded dimethyl phenylphosphonate and the nitro compound (37)[129] (Scheme 63).

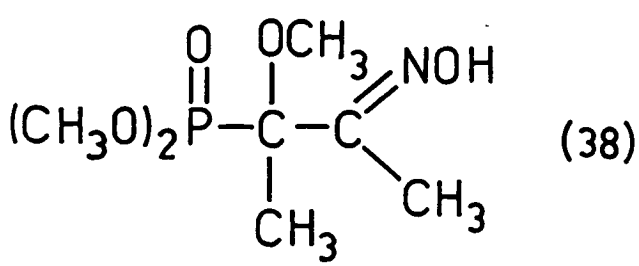


(36)

(37)

Scheme 63

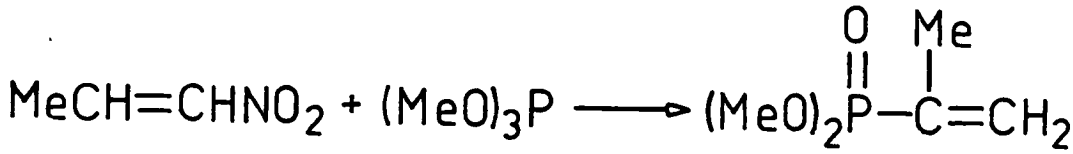
It has been found that the reaction of 2-nitrobut-2-ene with trimethyl phosphite gives the adduct at high concentrations of the reactants, while at lower concentrations the oxime (38) is formed.[130] The reaction of



(38)

nitroalkenes with tervalent phosphorus reagents has been studied under a variety of conditions. It has been found in many cases that the products are not the cyclic phosphoranes, but various open-chain compounds formed

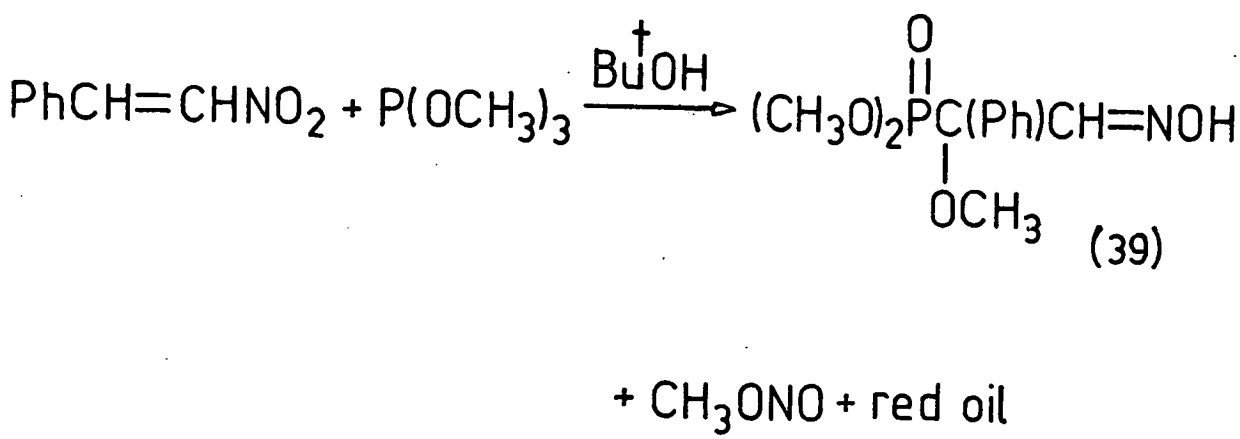
via a proton migration in the intermediate dipolar ion[131-135] (Scheme 64, for example[131]). It has been suggested[132] that the preferred



Scheme 64

cyclisation of the dipolar ion in the case of 2-nitrobut-2-ene[128] is due to the methyl group on the β-carbon atom stabilising the phosphorane due to its hyperconjugative effect, which also prevents a 1, 2-proton shift occurring in the intermediate dipolar ion.

Reaction of β-nitrostyrene with trimethyl phosphite in tert-butanol at room temperature has been found to give the oxime (39) (34%), together with methyl nitrite and a red oil[136] (Scheme 65). In a related reaction,

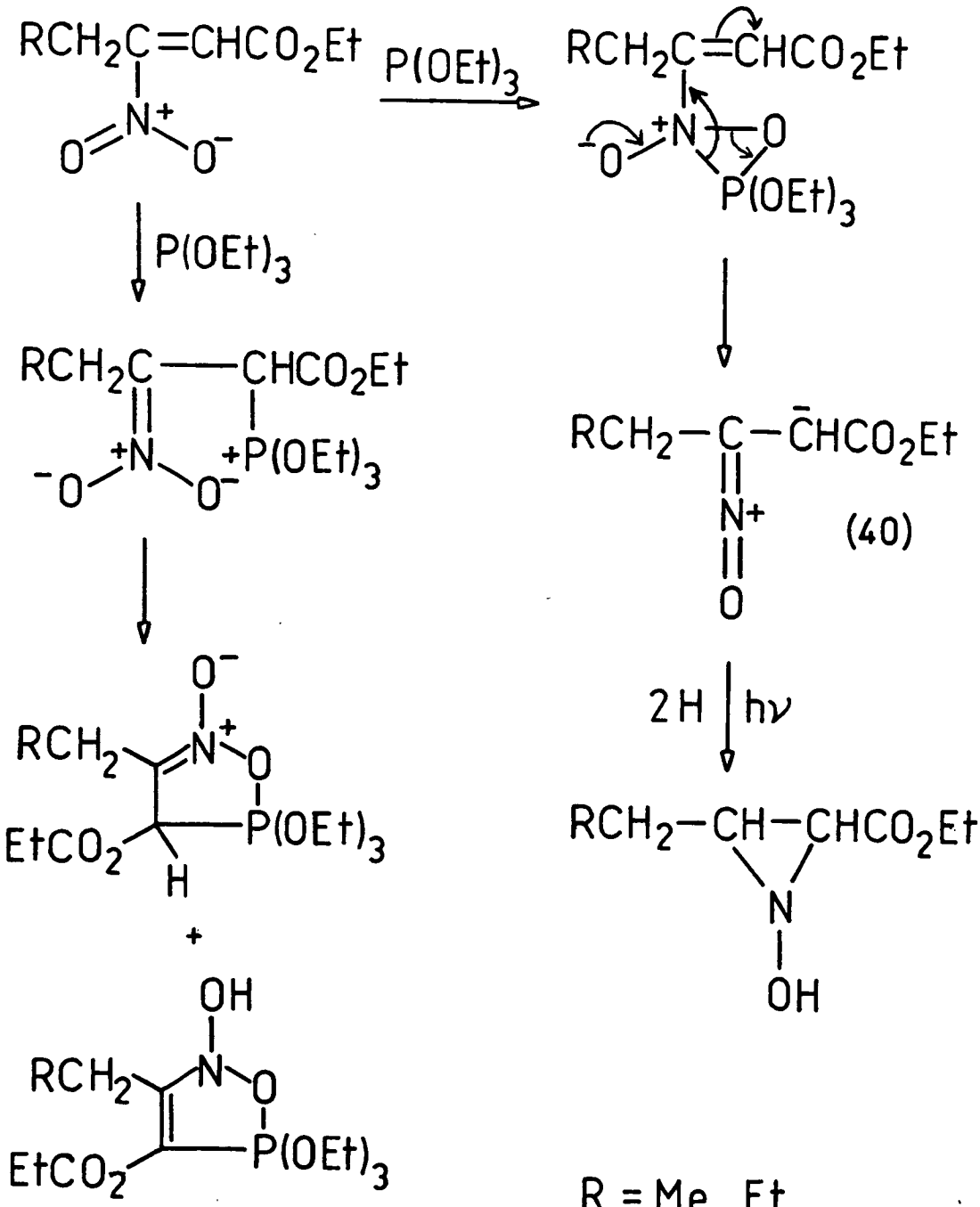


Scheme 65

Cadogan and co-workers[137] found that reaction of E -1,2-diaryl-1-nitroethenes with tervalent phosphorus reagents in tert-butanol gave the 2-oxo-1, 2, 5-oxazaphosph(v)oles. In this case, however, the phosphoranes were much more stable than the all-aliphatic ones already described.[128, 129]

Phosphoranes have also been claimed to be products of the reaction

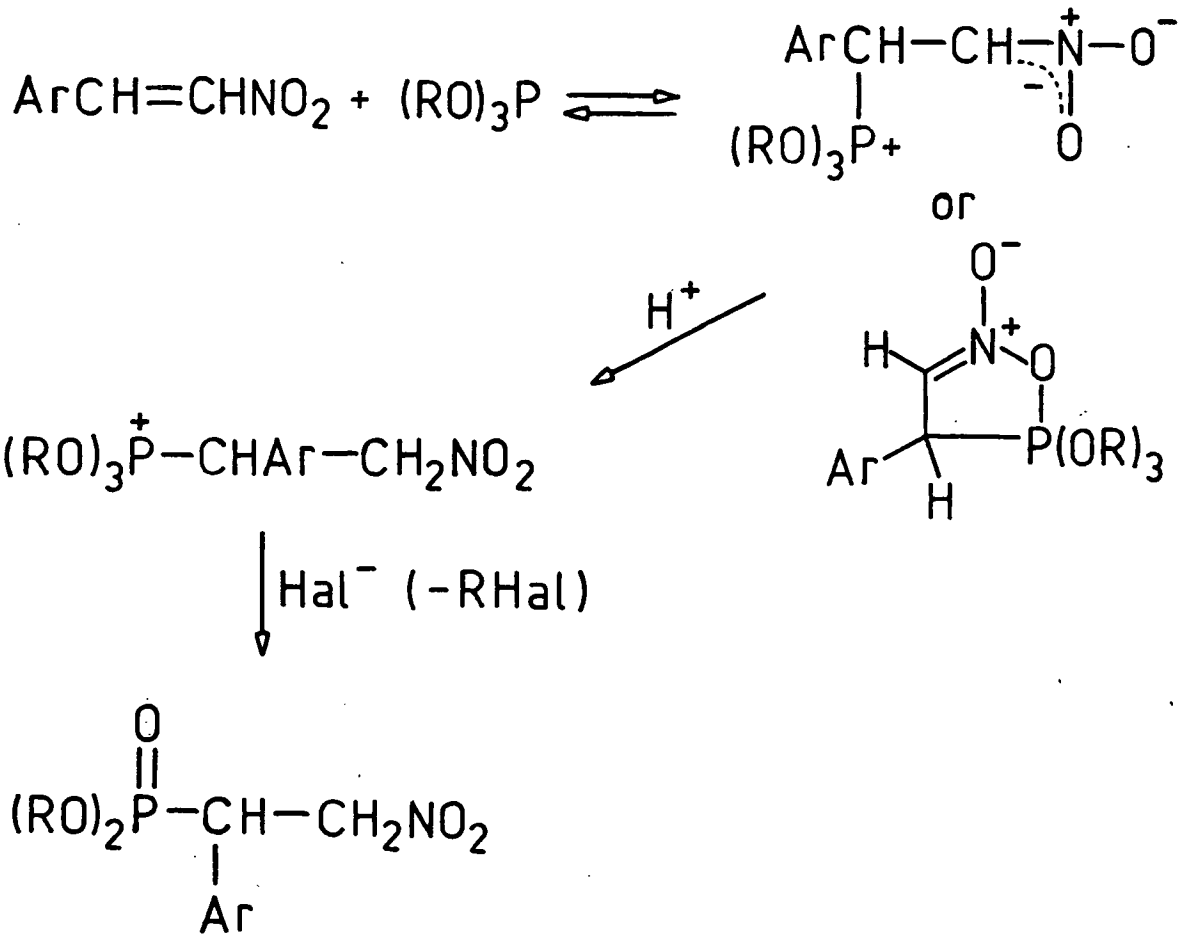
of ethyl α,β-unsaturated β-nitrocarboxylates with triethyl phosphite[138] (Scheme 66). A mixture of the two tautomers is said to be produced, but this has never been observed in any other case. In addition, the quoted




Scheme 66

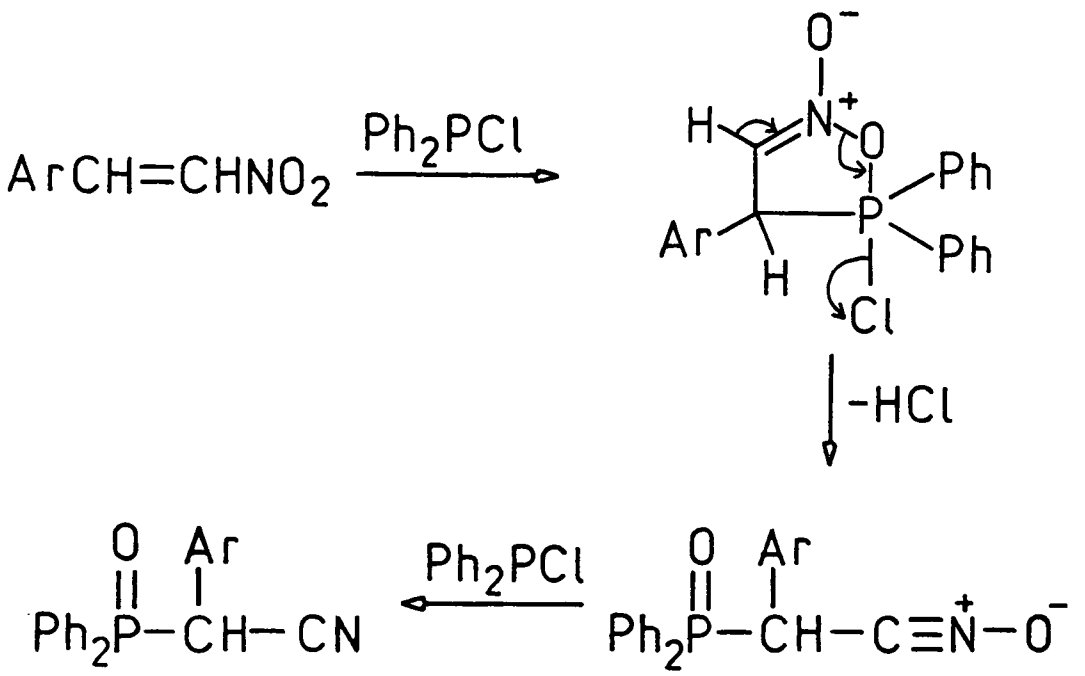
[31]P n.m.r. shifts of -208 and -215 p.p.m. are more typical of phosphorus

(VI) than phosphorus(V) species. The other product, the aziridine, is thought to arise by attack on the nitro group, proceeding via the intermediate (40) which shows an I. R. band at 2050 $cm^{-1}$. This intermediate would, however, be expected to undergo a rapid electron shift to give the nitrosoalkene, but this possibility is not commented on. This report must therefore be regarded with some scepticism. The same authors have reported[139] that the ethyl $\alpha,\beta$-unsaturated $\alpha$-nitrocarboxylates did not give the phosphorane, but it was postulated as an intermediate in the reactions. Other cases have been reported where phosphoranes are postulated as intermediates in the reaction of nitroalkenes with phosphorus (III) reagents. Reaction of $\beta$-nitrostyrenes with trialkyl phosphites gave rise to $\alpha$-aryl-$\beta$-nitroethanephosphonates by protic addition[140] (Scheme 67),



Scheme 67

and a similar reaction with diphenylphosphinous chloride could also be explained by invoking a phosphorane intermediate[141] (Scheme 68).

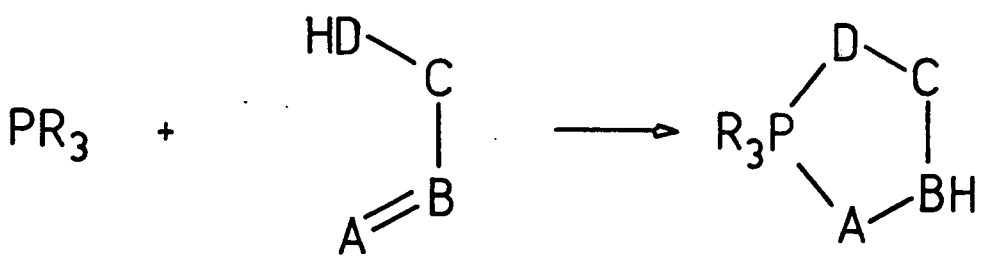


Scheme 68

B. 3 Miscellaneous Phosph(v)oles

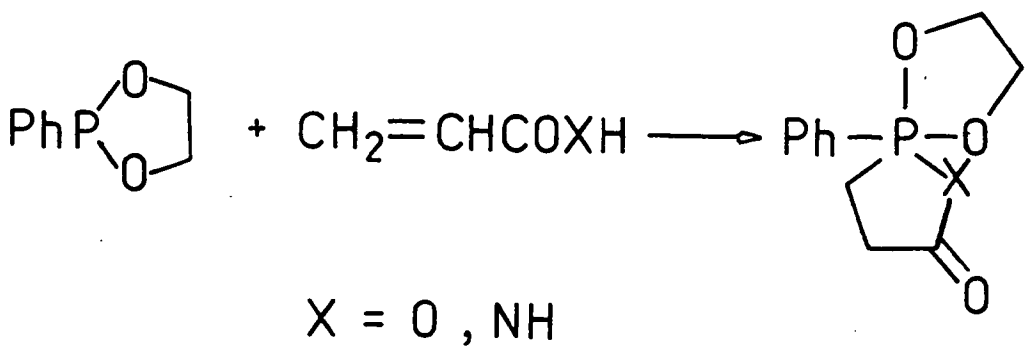
(a) Phosph(v)oles Derived from Unsaturated Systems via Hydrogen Transfer

A number of examples of this type of reaction are known. All can be represented by the general reaction below (Scheme 69), but there may be slight variations in individual cases.



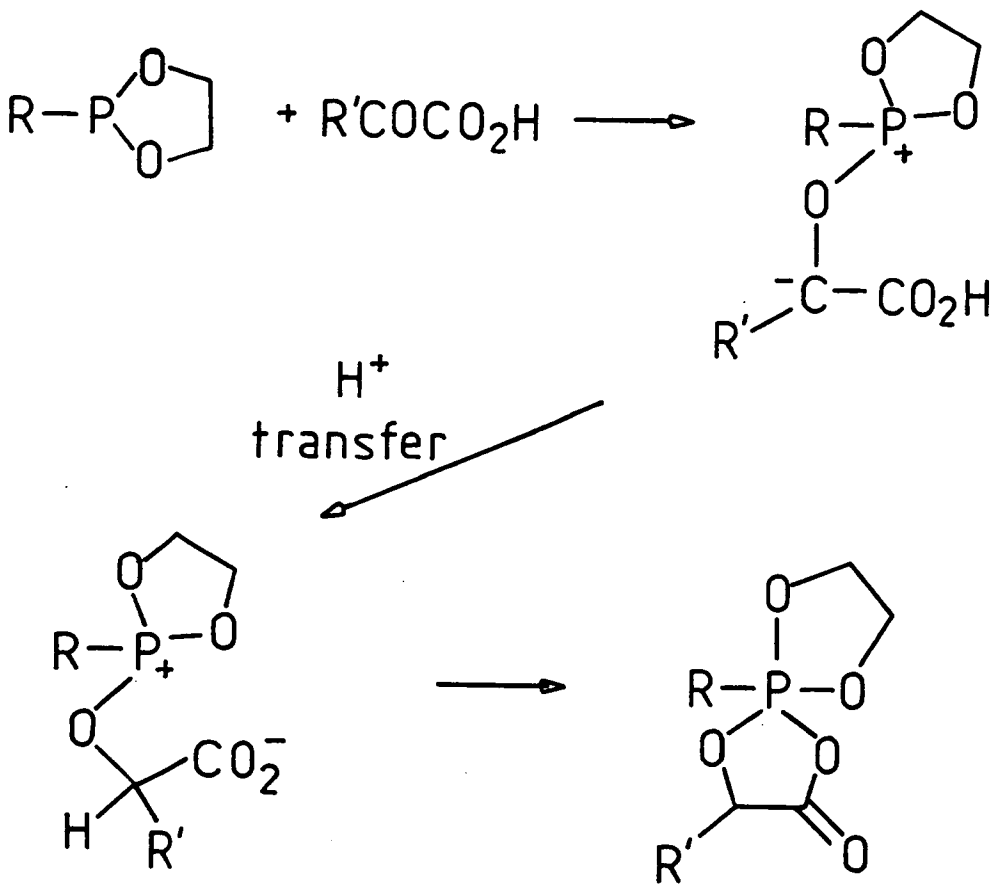
Scheme 69

Reaction of 2-phenyl-1, 3, 2-dioxaphospholan with acrylic acid and acrylamide gave the first examples of crystalline pentacovalent cyclic acyloxy- and amido-phosphoranes in good yield[142] (Scheme 70).




Scheme 70

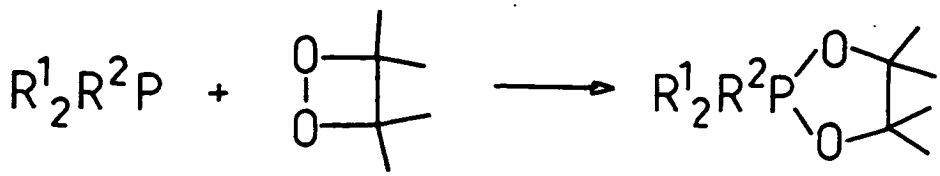
A similar acyloxyphosphorane was obtained from 2-hydroxycinnamic acid and methyl diphenylphosphinite, this time via a substitution intermediate[143] (cf. section B. 2(d)). This phosphorane was not very stable by comparison with the spirocyclic acyloxyphosphoranes above. Other examples of phosphoranes from $\alpha,\beta$-unsaturated acids have been reported.[144] Analogous reactions have been shown to occur with $\alpha$-keto acids.[145] It was proposed that the reaction involves an intermediate phosphonium carbanion which undergoes hydrogen transfer to give a zwitterion, which then ring closes (Scheme 71).




Scheme 71

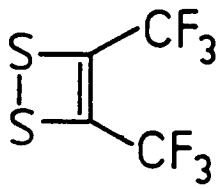
(b) Phosph(v)oles Derived from Compounds with Weak Sigma Bonds

Trivalent phosphorus compounds often react with substances with weak σ bonds to give pentacoordinate phosphorus compounds. Tetramethyl-1, 2-dioxetane reacted with triphenylphosphine,[146] and with trimethyl and triethyl phosphite, and methyl diphenylphosphinite[147] to give phosphoranes in good yield (Scheme 72). This reaction was used to produce a mixture of 3-membered ring phosphoranes by reacting 3, 3, 4-trimethyl-1, 2-dioxetane with phenylphosphiran at low temperature.[148] These



Scheme 72

phosphoranes are quite unstable and decompose with loss of ethylene on heating to room temperature. The related dithiete (41) also reacted

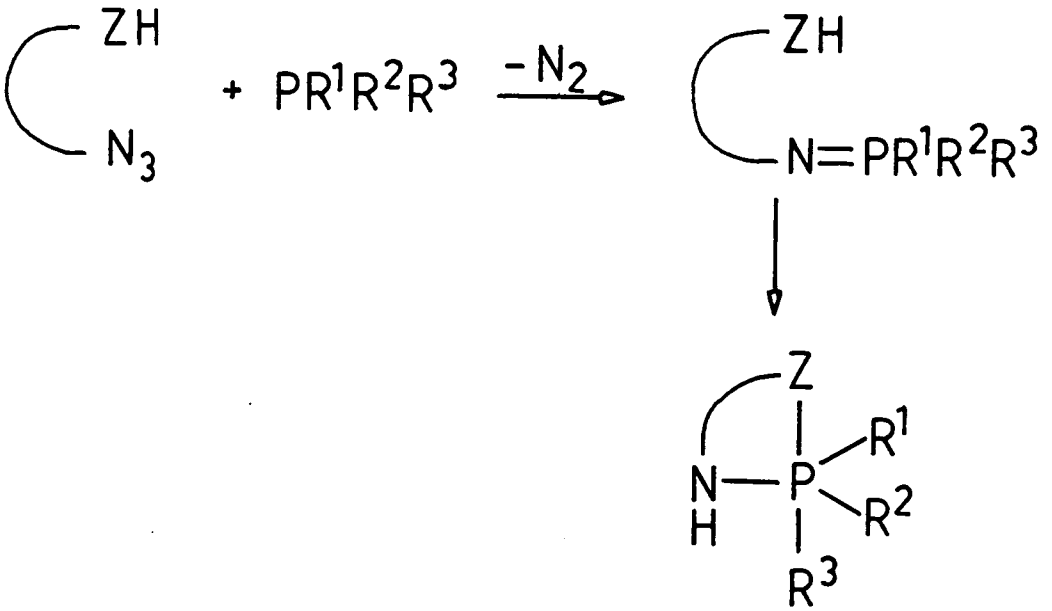


(41)

with tervalent phosphorus reagents to give phosphoranes in a number of cases.[149] In other cases, products were formed which were thought to arise from decomposition of the intermediate phosphorane. The phosphoranes did not appear to be as stable as their oxygen counterparts derived from hexafluorobiacetyl.

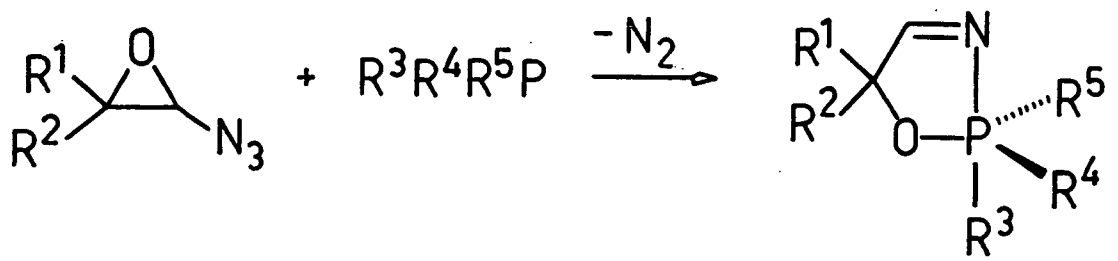
(c) Phosph(v)oles Derived from Azido Compounds

Phosphoranes have been obtained from o-azidoaromatic compounds and phosphorus(III) reagents.[150] A similar reaction has been observed with other bifunctional azido compounds such as α-azidobenzaldehyde, derivat 2-azido-1-phenylethanol, and 2-azidobenzyl alcohol.[151] The reaction proceeds via the formation of the iminophosphorane followed by intramolecular cyclisation via addition to the P=N group (Scheme 73). An analogous reaction involved formation of the iminophosphorane from 2-phenyl-1, 3, 2-dioxaphospholan and phenyl azide, followed by intermolecular addition of a diol, leading to the phosphorane by displacement of aniline.[152]



Scheme 73

High yields of 2, 5-dihydro-1, 3, 2-oxazaphosph(v)oles have been produced by reaction of 2-azido-oxirans with tervalent phosphorus reagents[153] (Scheme 74). These exhibit a trigonal bipyramidal structure with the $sp^2$

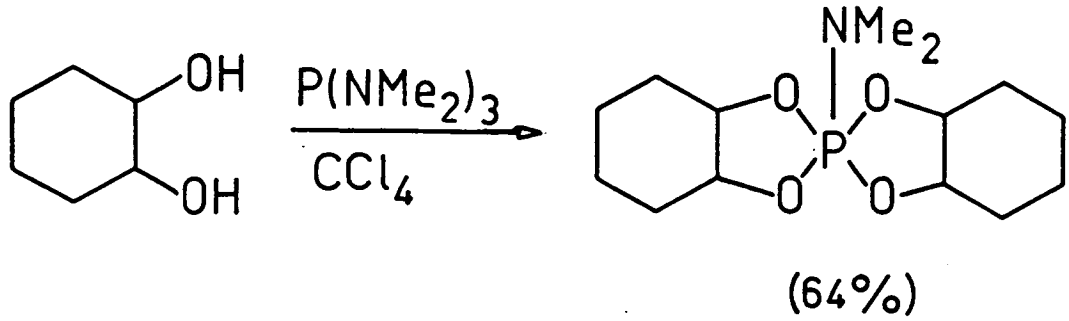


Scheme 74

nitrogen atom apical and the oxygen atom equatorial.

(d) Phosph(v)oles Prepared from Diols

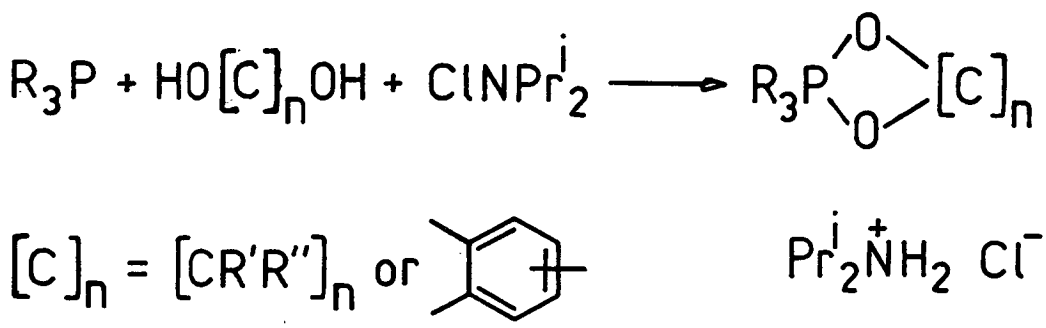
This is a very common reaction, and some examples have already been discussed. 1, 2-Diols are most commonly employed in these reactions. For example, reaction of vicinal diols, such as cis-cyclohexane diol, with tris(dimethylamino)phosphine and carbon tetrachloride has resulted in the formation of spirophosphoranes[154] (Scheme 75). A 2', 3'-phosphorane




(64%)

Scheme 75

was the result of the reaction of adenosine with triphenyl phosphine/diethyl azodicarboxylate.[155] Trippett[156] has developed a useful general method of preparing phosphoranes by the condensation of cyclic or acyclic tervalent phosphorus reagents with 1, 2- or 1, 3-diols, or with catechols in the presence of N-chlorodi-isopropylamine (Scheme 76). The product



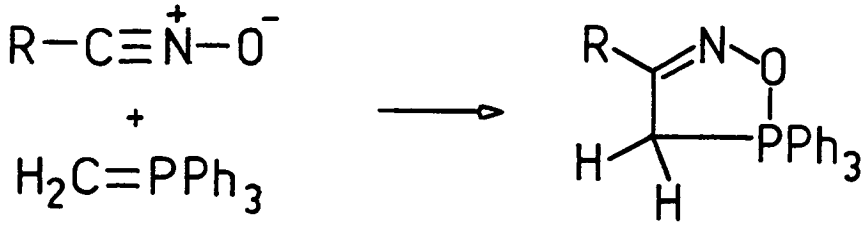

Scheme 76

can be easily isolated in high yield by filtration and evaporation of the solvent ether. The method can be extended to other systems.[157]

(e) 1, 2, 5-Oxazaphosph(v)oles

The 2-oxo-1, 2, 5-oxazaphosph(v)oles have already been discussed as the products of the reaction of nitroalkenes with phosphorus(III) reagents. The corresponding system lacking the N-oxide function has also been investigated in detail. Bestmann and Kunstmann[158] isolated an adduct from the reaction of benzonitrile oxide with isopropylidenetriphenyl-

phosphorane, and suggested it had an open-chain dipolar structure. Huisgen,[159, 160] however, showed that the crystalline adducts from benzonitrile oxides and methylenetriphenyl phosphorane existed in the cyclic 1, 2, 5-oxazaphosph(v)ole form (Scheme 77), the crucial evidence being the negative $^{31}P$ n.m.r. shifts.

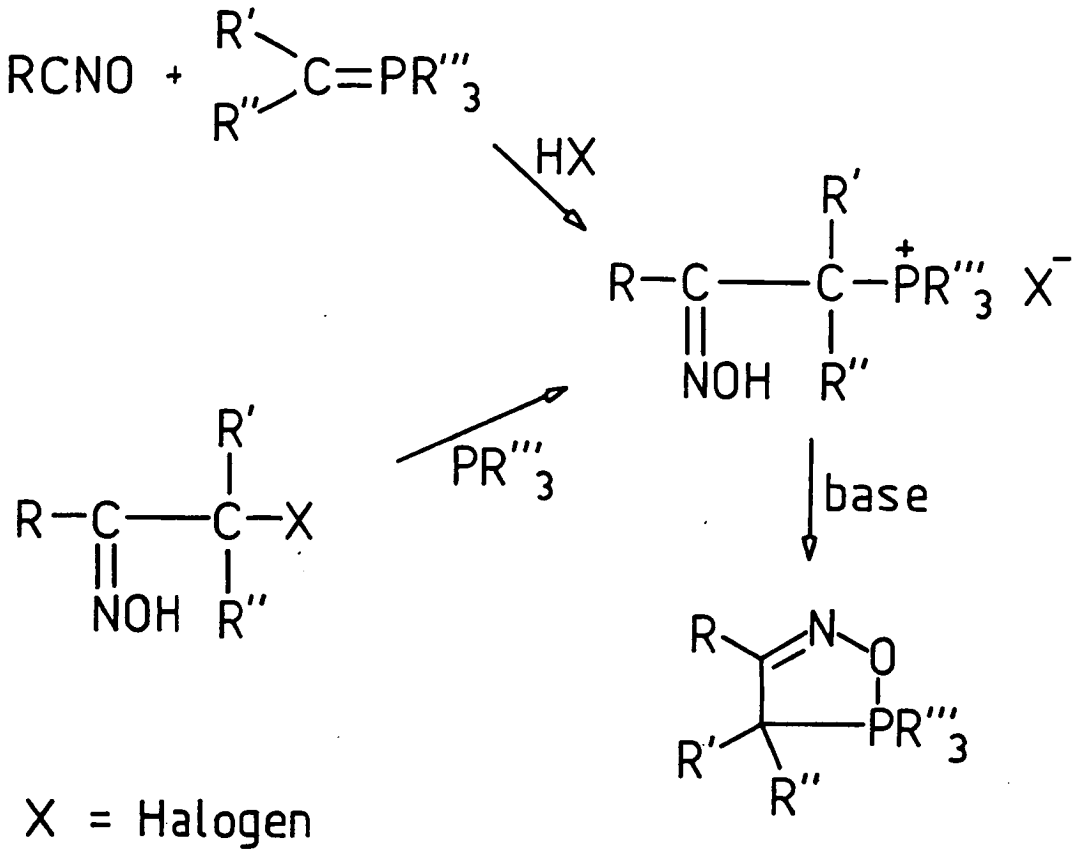



R = Ph ; 2,4,6-trimethylphenyl

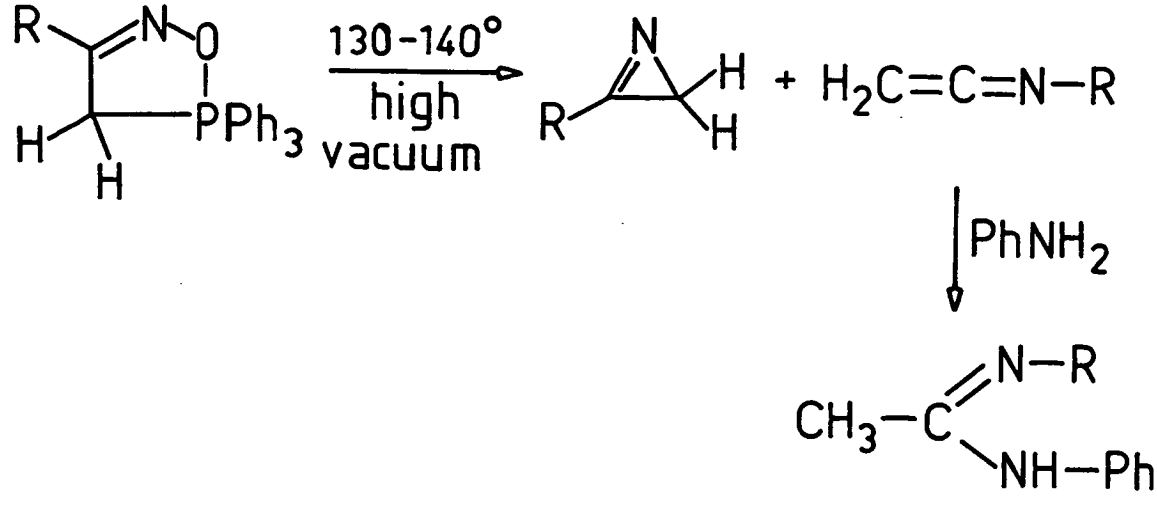
Scheme 77

Other examples of phosphorane formation from ylides and nitrile oxides have been reported.[161, 162] Another route to the phosph(v)oles involves initial formation of 2-oximinophosphonium salts which are then cyclised in high yield by treatment with base.[163-165] The salts are obtained by reaction of nitrile oxides with phosphorus ylides in dimethyl sulphoxide followed by acidic work-up, or more conveniently by reaction of α-halo ketoximes with phosphines or by oximation of the corresponding 2-keto-phosphonium salts (Scheme 78). The cyclisation step is best performed by a basic ion exchange resin,[163, 164] although aqueous sodium or potassium hydroxide[164, 165] can also be used. The ring closure is reversed by acid.

It has been shown that thermolysis of these phosph(v)oles leads to azirines[159-161, 164] and/or ketenimines[159-161] (Scheme 79, for example). A detailed investigation[161] has been carried out on the effect on the thermolysis products of varying the substituents in the oxazaphosph(v)ole




Scheme 78

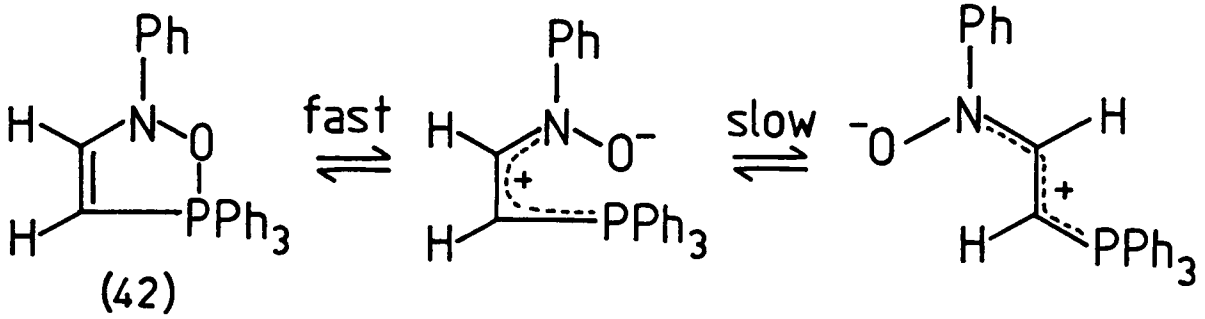



Scheme 79

ring. It was found that the relative amounts of azirine and ketenimine depended on the substituents, and, in general, when R′ (Scheme 78) was electron-withdrawing, the ketenimine was favoured.

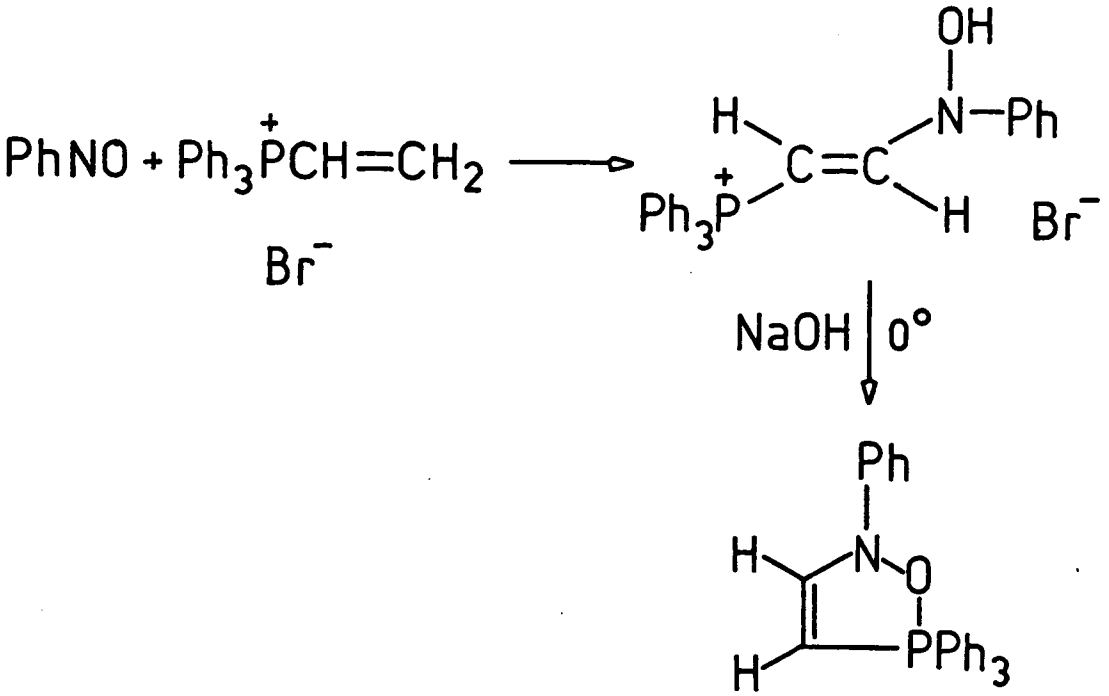
The possibility of a co-existent betainic structure for the phosph(v)oles

has been suggested,[165] and Howe[166] has shown this to be the case for the related phosphorane (42). This exists solely in the cyclic form in carbon tetrachloride, $d_6$-benzene, and toluene, but in $CDCl_3$ and alcohols it is an equilibrium mixture of cyclic and open-chain dipolar forms (Scheme 80). The phosphorane is formed by basic treatment of the product from




Scheme 80

the reaction of nitrosobenzene with triphenylvinylphosphonium bromide (Scheme 81).



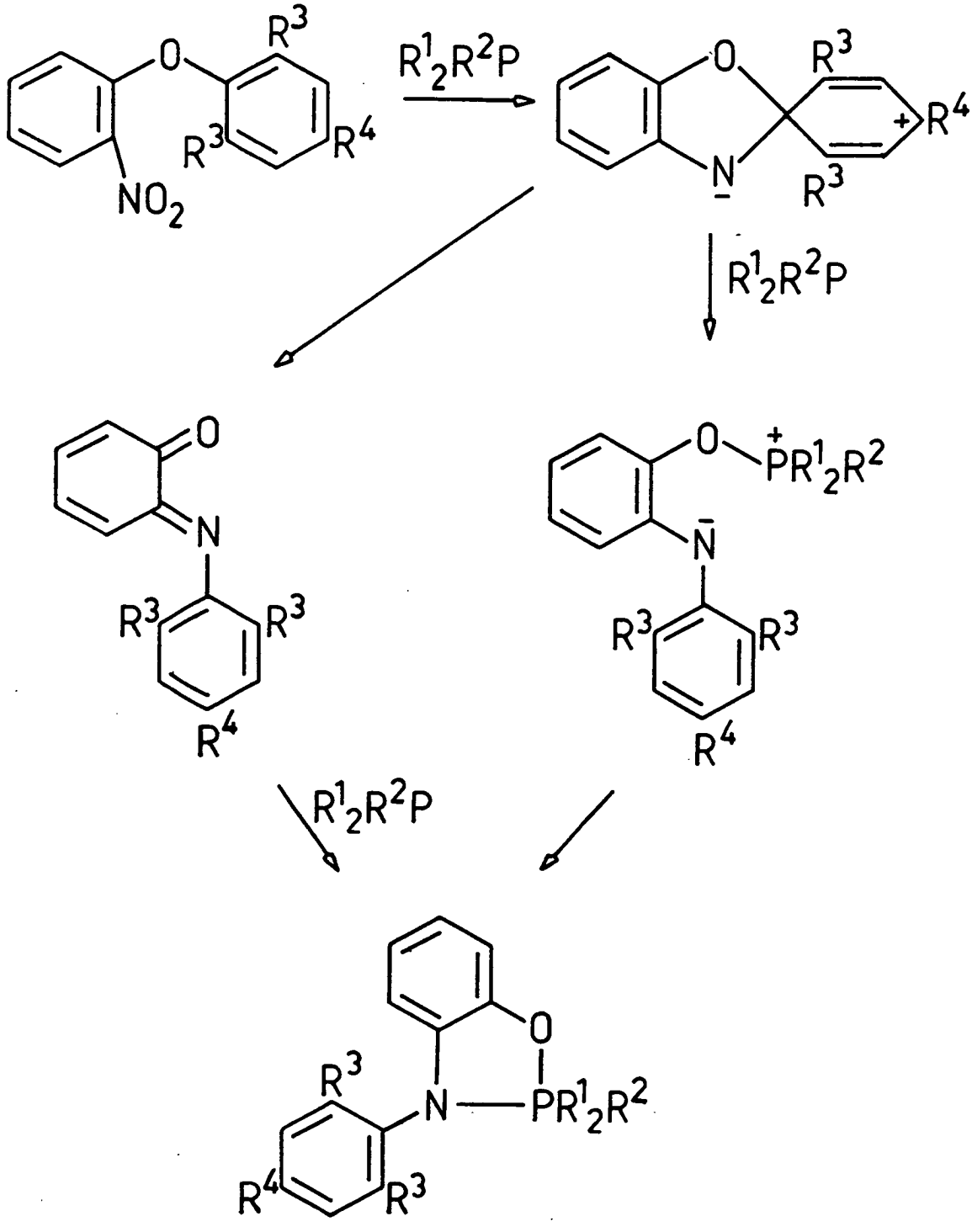

Scheme 81

Phosphoranes containing a fully saturated 1, 2, 5-oxazaphosph(v)ole

ring system have been prepared by the analogous reaction of phosphorus ylides with nitrones.[167]

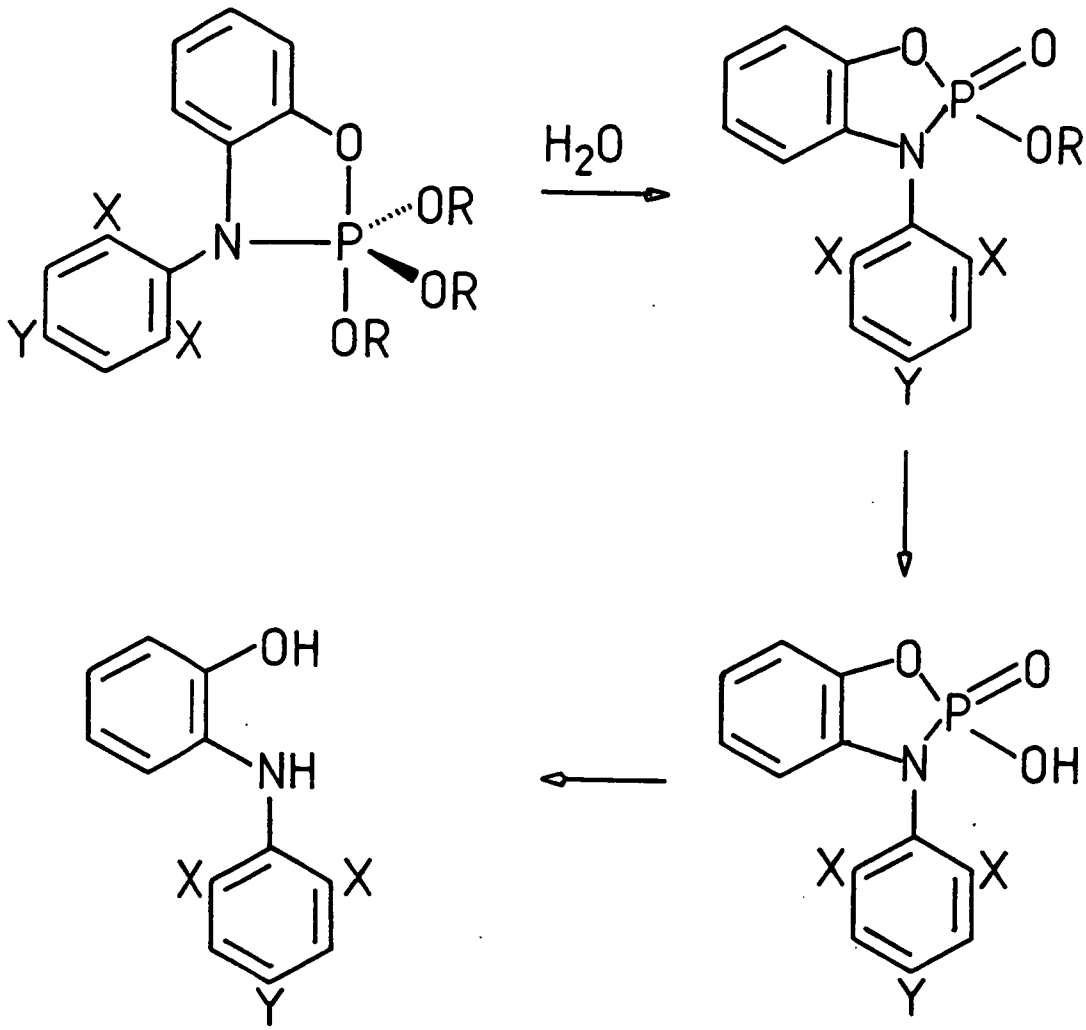
(f) 3-Aryl-2, 3-dihydro-1, 3, 2-benzoxazaphosph(v)oles and Related Compounds

Cadogan and co-workers[168, 169] have found that reaction of aryl 2-nitroaryl ethers with tervalent phosphorus reagents in cumene gives the novel 3-aryl-2, 3-dihydro-1, 3, 2-benzoxazaphosph(v)oles (12-95%). A mechanism involving a spiro-diene intermediate has been postulated (Scheme 82). The structure of the phosphoranes has been confirmed by X-ray crystallography.[170] Detailed $^{1}H$ n. m. r. studies have also been carried out on the phosphoranes.[171]



Scheme 82

Hydrolysis of the phosphoranes can lead to three different products depending on the conditions[169] (Scheme 83). The final product in acid solution is the o-hydroxydiphenylamine. The phosphoranes also undergo

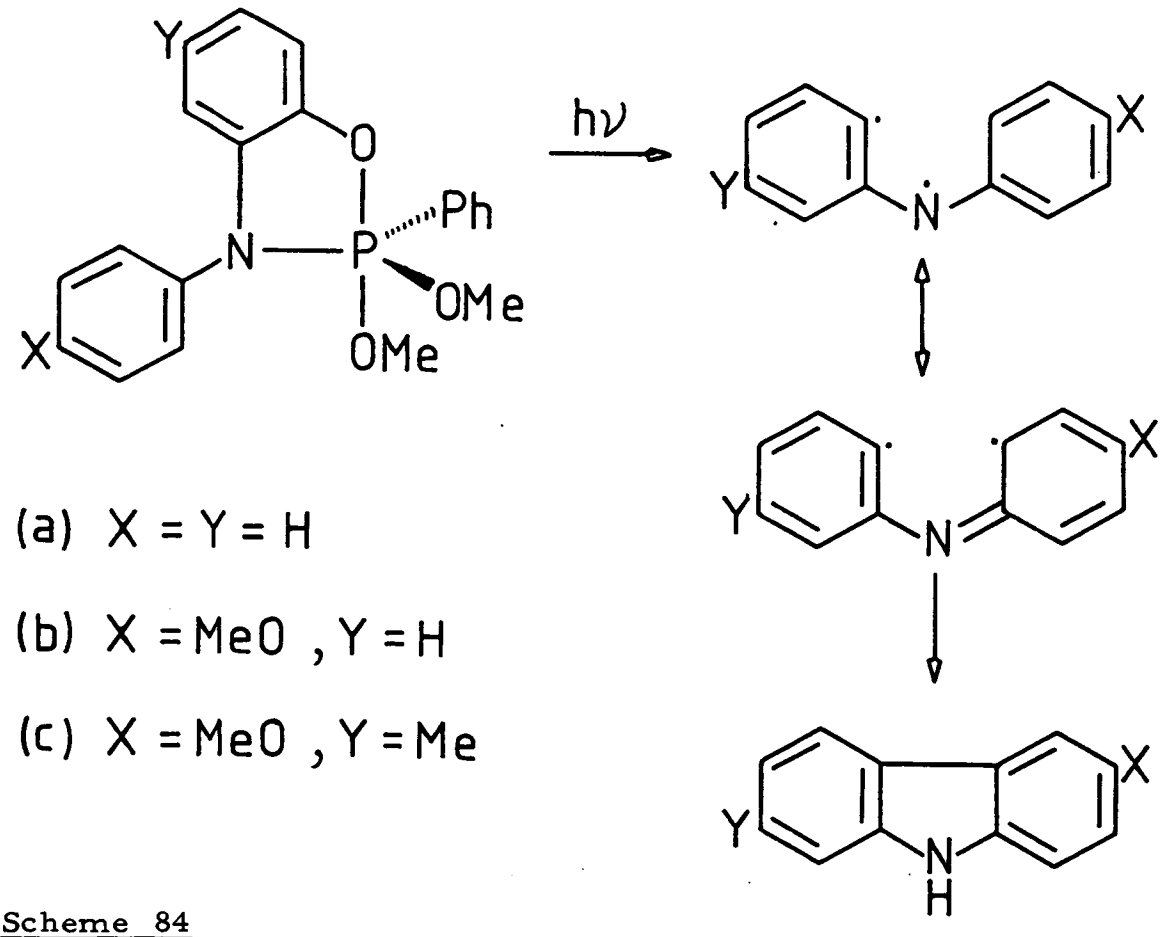



Scheme 83

ligand exchange with diols.[169]

Photolysis of the phosphoranes leads to loss of dimethyl phenylphosphonate and formation of the carbazole, presumably via a diradical[172] (Scheme 84).

The formation of phenothiazines by deoxygenation of aryl 2-nitrophenyl sulphides[69] has already been discussed (Section A. 3(d)). It has been found that when the ortho positions are blocked, good yields of phosphoramidates are obtained and this was taken as evidence for the intermediacy of 2, 3-dihydro-1, 3, 2-benzothiazaphosph(v)oles[173] (Scheme 85). The formation of heterocyclic by-products in the sulphur case is in accord

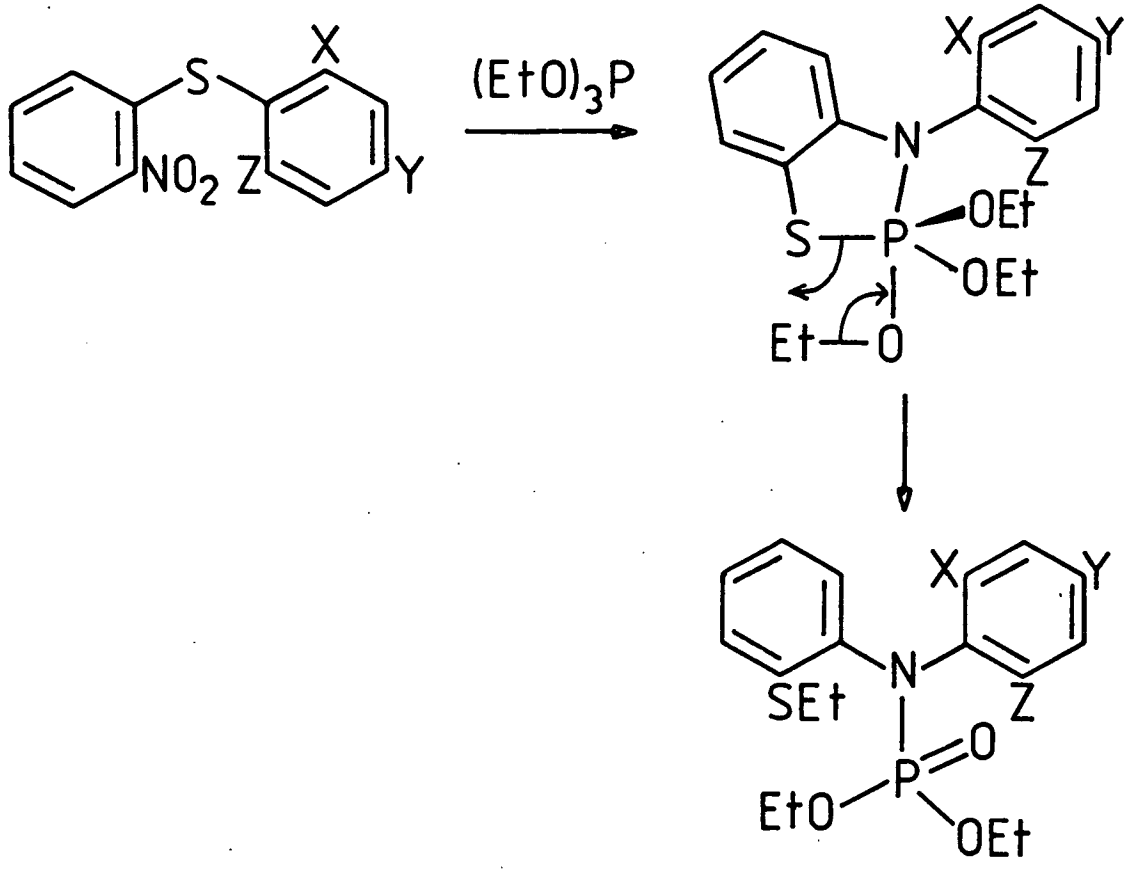



(a) X = Y = H

(b) X = MeO , Y = H

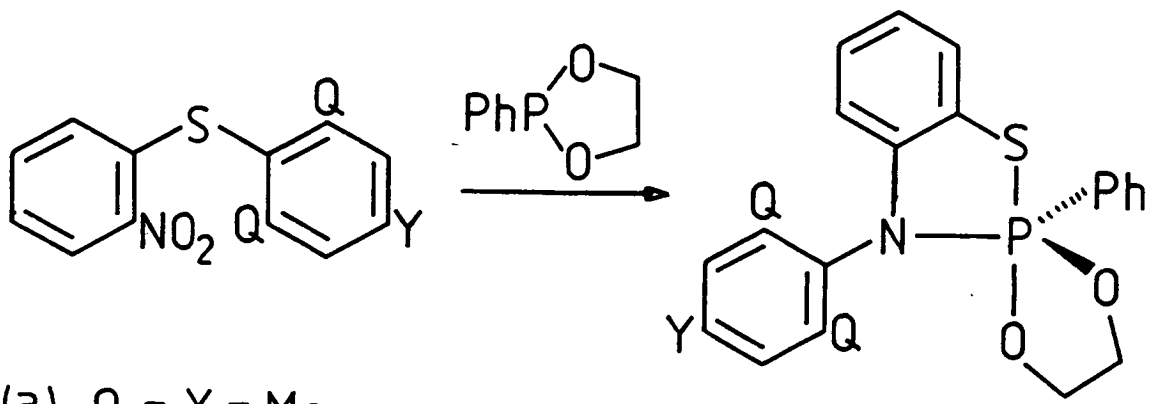
(c) X = MeO , Y = Me

Scheme 84




Scheme 85

with the greater migratory aptitude of sulphur than oxygen. Spiro-amino(thiyl)phosphoranes (43) have now been isolated in 32-76% yield using 2-phenyl-1, 3, 2-dioxaphospholan as the deoxygenating agent[174] (Scheme 86). The structure of (43b) has been confirmed by X-ray crystallography.[175]




(a) Q = Y = Me

(b) Q = Me , Y = H

(c) Q = MeO , Y = H

(43)

Scheme 86

# Experimental

## A. Symbols and Abbreviations

| | |
|---|---|
| b. p. | boiling point |
| m. p. | melting point |
| tlc | thin-layer chromatography |
| glc | gas liquid chromatography |
| h. p. l. c. | high pressure liquid chromatography |
| lplc | low pressure liquid chromatography |
| n. m. r. | nuclear magnetic resonance |
| s; d; t; q; m | singlet; doublet; triplet; quartet; multiplet |
| J | coupling constant |
| $\delta$ | chemical shift |
| I. R. | infra-red |
| $M^+$ | mass of molecular ion |
| m/e | mass to charge ratio |
| $m^*$ | metastable peak |
| h; min; s; | hours; minutes; seconds |
| p. p. m. | parts per million |
| mmol | millimoles |
| U. V. | ultra-violet |

B. Instrumentation

Melting Points. Melting points of new compounds were obtained on a Kofler hot-stage apparatus. All others were obtained using capillary tubes and Gallenkamp apparatus.

Nuclear Magnetic Resonance Spectroscopy

(a) Routine $^{1}H$ n.m.r. spectra were recorded on a Varian EM360 spectrometer. 100 MHz spectra of new compounds were obtained using a Varian HA 100 spectrometer operated by Mr. J. Miller. 360 MHz spectra were recorded by Dr. I. H. Sadler using a Bruker WH 360 spectrometer. Chemical shifts ($\delta_H$) are measured in parts per million relative to tetramethylsilane (T.M.S.) as standard ($\delta = 0.0$).

(b) $^{31}P$ N.m.r. spectra were recorded principally on a Jeol FX 60 spectrometer, and in a few cases, on a Varian XL 100 spectrometer operated by Dr. A. Boyd. Chemical shifts ($\delta_P$) are measured in p.p.m. relative to 85% external phosphoric acid ($\delta = 0.0$). Shifts to high frequency of the standard are positive. Where appropriate, the relative peak areas in arbitrary units (%) are given in brackets, usually following the chemical shift.

(c) $^{13}C$ N.m.r. spectra were generally recorded on a Varian CFT 20 spectrometer operated by Mr. J. Miller, and in a few cases, on a Varian XL 100 spectrometer or a Bruker WH 360 spectrometer operated respectively by Dr. A. Boyd and Dr. I. H. Sadler. Chemical shifts ($\delta_C$) are measured in p.p.m. relative to T.M.S. ($\delta = 0.0$).

Infra-red Spectroscopy. I.R. spectra were recorded on a Perkin-Elmer

157G Grating Spectrophotometer. Liquid samples were recorded as thin films, and solid samples as nujol mulls (if not otherwise stated) or in solution in chloroform.

Ultra-violet Spectroscopy. U. V. spectra were recorded on a Unicam SP 800 spectrophotometer. Solutions of samples were prepared in absolute ethanol.

Mass Spectroscopy. Mass spectra and exact masses were obtained on an AEI MS 902 mass spectrometer operated by Mr. D. Thomas.

Elemental Analysis. Microanalyses of all new compounds were obtained using a Perkin-Elmer model 240 analyser operated by Mr. J. Grunbaum.

Gas-liquid Chromatography. Qualitative glc analysis was carried out using a Pye Series 104 chromatograph with a flame ionisation detector.

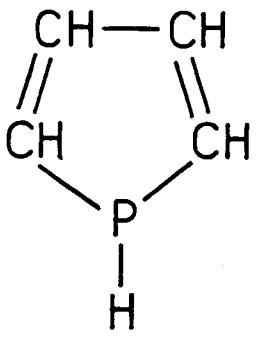
High Pressure Liquid Chromatography. Qualitative h. p. l. c. analysis was carried out using a 0. 5 cm diameter polished stainless steel column packed with 5 micron Spherisorb silica, and coupled to a Cecil Instruments CE 12 U. V. monitor which served as the detector.

Low Pressure Liquid Chromatography. Preparative chromatography using pressurised eluants was carried out using glass columns and fittings supplied by Jobling, and 50 micron silica as the column packing. A U. V. detector by Laboratory Data Control was used to monitor the output from the column to the fraction collector.

Thin-layer Chromatography. Chromatograms were developed on 0. 33 mm layers of alumina (Merck, Aluminium Oxide G) or silica gel (Merck, Silica Gel G) containing Woelm fluorescent green indicator (0. 5%). Components of the chromatogram were detected by their quenching of fluorescence under U. V. light, or by their absorption of iodine.

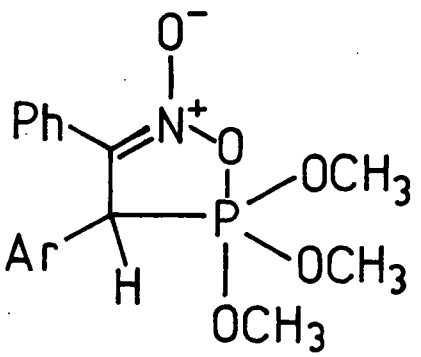
C. Nomenclature

Compounds in which the phosphorus atom is part of an unsaturated five-membered ring are named as derivatives of phosphole (44). In cyclic



(44)

phosphoranes, where the phosphorus is pentacoordinate, this is indicated by the insertion of (v) viz. phosph(v)ole. When additional heteroatoms are incorporated in the ring, the locant 1 is assigned to the heteroatom of highest priority, the order of priority being O > S > N > P. The remaining heteroatoms are then assigned the lowest possible numbers. The phosphoranes considered here are members of the 1, 2, 5-oxazaphosph(v)ole ring system, and structure (45) may serve as an example of the nomenclature employed. The ring is not fully unsaturated and this is represented by the use of the term "dihydro." This compound is named 4-aryl-4, 5-dihydro-



(45)

5, 5, 5-trimethoxy-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

D. Preparation of Materials

(a) Ether and hexane were dried over sodium wire. Petrol ether (40-60) and benzene were redistilled and dried over sodium wire. t-Butylbenzene was distilled from lithium aluminium hydride and stored over molecular sieve. Dimethyl sulphoxide was distilled from calcium hydride and stored over molecular sieve. Methanol was distilled from magnesium methoxide and stored over molecular sieve. Chloroform and dichloromethane were passed down an alumina column and stored over calcium chloride. Triethylamine was redistilled and stored over sodium hydroxide and molecular sieve. Where necessary, solutions were dried over anhydrous magnesium sulphate, unless otherwise stated. All other reagents were recrystallised or redistilled as necessary.

(b) Triethyl and Trimethyl Phosphite were allowed to stand over sodium wire for 24 h, then redistilled and stored over molecular sieve.

(c) Dimethyl Phenylphosphonite was prepared by reaction of dichlorophenylphosphine (106.8 g, ; 0.6 mol) with methanol (48 g; 1.5 mol) in the presence of triethylamine (153 g; 1.5 mol), with ether (975 ml) as the solvent.[176] The product was obtained as a colourless liquid (54.8 g; 54%), b.p. 86-88°C/10 mm (lit[177] 101-102°C/15 mm) after two distillations under dry nitrogen. The purity was confirmed by n.m.r. $\delta_P$ ($CDCl_3$): +160.7 p.p.m.

(d) Methyl Diphenylphosphinite was prepared by the method of Quin and Anderson.[178] Reaction of diphenylphosphinous chloride (22.1 g; 0.1 mol)

with methanol (4 g; 0.125 mol) in the presence of triethylamine (12.6 g; 0.125 mol) with ether (100 ml) as the solvent gave methyl diphenylphosphinite (15.6 g; 72%), b.p. 109-112°C/0.9 mm (lit[177] 151-152°C/10 mm) as a colourless liquid. $\delta_P$ ($CDCl_3$): +117.0 p.p.m.

(e) Nitrosyl Chloride was prepared by the reaction of a solution of sodium nitrite (103.5 g; 1.5 mol) in water (150 ml) with concentrated hydrochloric acid (600 ml; 7.2 mol).[179] The nitrosyl chloride (29.6 g; 30%) was stored as a 24% w/v solution in chloroform

(f) 1-Chloro-1, 2-diphenyl-2-nitrosoethane Dimer was prepared by nitrosochlorination of stilbene.[180] Reaction of trans-stilbene (5.40 g; 30 mmol) in chloroform (30 ml) with a chloroform solution (24% w/v) of nitrosyl chloride (2.0 g; 30 mmol) at -30°C gave the product as a white amorphous solid (4.96 g; 67%), m.p. 139-140°C, decomp. (lit[180a] 138-139°C). (Found: C, 66.2; H, 4.7; N, 5.1%. Calculated for $(C_{14}H_{12}ClNO)_2$: C, 68.4; H, 4.9; N, 5.7%).

(g) *α*-Benzoin Oxime was prepared by the method of Werner and Detscheff.[181] A solution of hydroxylamine hydrochloride (8 g; 0.11 mol) in water (20 ml) was neutralised with sodium hydroxide (4.4 g; 0.11 mol) in water (10 ml) and added to a mixture of benzoin (10 g; 0.047 mol) and commercial alcohol (50 ml). The mixture was heated under reflux for 1.5 h and worked up to give *α*-benzoin oxime (6.34 g; 60%), m.p. 152-154°C (lit[181] 151°C).

(h) Desyl Chloride was prepared according to the method of Fieser and Okumura.[182] Benzoin (4 g; 19 mmol) was reacted with thionyl chloride (4 ml; 55 mmol) at reflux temperature. Subsequent work-up and recrystallisation from ethanol gave desyl chloride (2.68 g; 62%), m.p. 64-66°C

(lit[182] 66-67°C).

(i) Desyl Bromide was prepared by the method of Patai and co-workers.[183] Reaction of deoxybenzoin (14 g; 71 mmol) with bromine (11.4 g; 71 mmol) in glacial acetic acid (160 ml) at 90-100°C led to the isolation of desyl bromide (10.9 g; 56%), m.p. 53-55°C (lit[183] 53°C).

(j) Phenylbenzyl Ketimine was prepared by the method of Campbell.[184] Benzylmagnesium chloride, prepared by reaction of benzyl chloride (55 ml; 0.44 mol) with magnesium turnings (9.5 g; 0.4 mol) in ether (200 ml), was reacted with benzonitrile (12 ml; 0.12 mol). Work-up yielded the ketimine hydrochloride (9.11 g; 33%) as a light yellow solid, m.p. 181-185°C, decomp. (lit[184] 210-211°C, decomp). Treatment of the hydrochloride with ammonia then gave the free base (3.82 g; 16%), m.p. 54-56°C (lit[184] 57°C).

(k) Silver Carbonate on Celite Reagent was prepared by the method of Fetizon and Golfier.[185] To a solution of silver nitrate (17 g; 0.1 mol) in distilled water (100 ml) was added celite (15 g) with vigorous stirring. A solution of sodium carbonate decahydrate (15 g; 0.52 mol) in distilled water (150 ml) was then added and the resultant yellow-green solid (28.1 g) filtered off, washed, and dried.

(l) Silver Tosylate was prepared by the method of Emmons and Ferris.[186] Silver oxide (4.98 g; 43%) was prepared by reaction of a concentrated aqueous solution of silver nitrate (8.50 g; 50 mmol) with a dilute aqueous solution of sodium hydroxide (2.07 g; 52 mmol). Reaction of the silver oxide (4.93 g; 21 mmol) with a solution of p-toluene sulphonic acid monohydrate (7.61 g; 40 mmol) in acetonitrile (70 ml) resulted in the formation of silver tosylate (10.61 g; 95%).

(m) Benzoin Tosylate was prepared by the method of Wilson and Sheehan.[187] A solution of silver tosylate (8.0 g; 29 mmol) in acetonitrile (45 ml) was treated with desyl bromide (7.5 g; 27 mmol) and the mixture heated on a steam bath for 20 min. Subsequent work-up yielded benzoin tosylate (8.14 g; 82%) as a white solid, m.p. 103-106°C (lit[187] 107-108.5°C).

(n) Benzytriphenylphosphonium Chloride was prepared by reaction of triphenylphosphine (26.2 g; 0.1 mol) with benzyl chloride (17.0 g; ca 0.13 mol) in refluxing acetonitrile (70 ml).[188] The product (36.4 g; 94%) precipitated as white crystals, m.p. 314-317°C, decomp. (lit[189] 325-330°C). $\delta_P$ ($CDCl_3$): +23.2 p.p.m.

(o) Methyl Nitrate was prepared by the method of Black and Babers[190] by the cautious addition of a mixture of methanol (119 g; 150 ml; 3.7 mol) and concentrated sulphuric acid (92 g; 50 ml) to a mixture of concentrated nitric acid (425 g; 300 ml; 4.6 mol) and concentrated sulphuric acid (550 g; 300 ml). The ester (211.5 g; 74%) was obtained as a nearly colourless oil.

(p) Phenylnitromethane was prepared by the method of Black and Babers.[191] Sodium ethoxide was prepared from sodium (46 g; 2 mol) and absolute ethanol (600 ml). To this was added a mixture of benzyl cyanide (234 g; 2 mol) and methyl nitrate (211.5 g; 2.75 mol) resulting in the formation of sodium phenyl-aci-nitroacetonitrile (252.0 g; 69%) as a white solid. This was added to a boiling solution of sodium hydroxide (300 g) in water(1200 ml), the resultant solid mixed with ice (500 g) and reacted with concentrated hydrochloric acid (800-900 ml) to give phenylnitromethane (131.4 g; 48% based on benzyl cyanide) as a light yellow oil, b.p. 70-72°C/0.6 mm (lit[191]

90-92°C/3 mm).

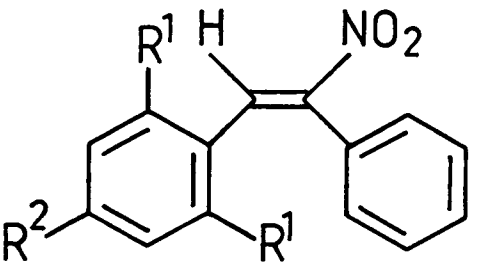
(q) p-Cyanobenzaldehyde was prepared by the method of Hass and Bender.[192] To a solution of sodium (3.45 g; 0.15 mol) in absolute ethanol (150 ml) was added 2-nitropropane (17.4 g; 0.195 mol) followed by α-bromo-p-tolunitrile (29.4 g; 0.15 mol). Sublimation (55°C/0.05 mm) of the crude product yielded p-cyanobenzaldehyde (9.25 g; 47%) as a white solid, m.p. 94-96°C (lit[192] 95-96°C); $\nu_{max}$ 2230 and 1705 $cm^{-1}$.

(r) 2-Aryl-1-phenylnitroethenes (α-nitrostilbenes) were prepared by the method of Robertson.[193] The general method is illustrated by the preparation of 2-(4-cyanophenyl)-1-phenylnitroethene. A solution of p-cyanobenzaldehyde (9.18 g; 70 mmol) and n-butylamine (5.12 g; 70 mmol) in benzene (25 ml) was heated under reflux in a flask fitted with a Dean and Stark water trap. After the correct theoretical amount of water (1.26 ml) had been collected, the benzene was removed under reduced pressure to leave the Schiff's base. This was then added to a solution of phenylnitromethane (9.60 g; 70 mmol) in glacial acetic acid (18 ml). After a few days at room temperature, a crystalline solid was formed, and this was filtered off and washed with water. Recrystallisation from ethanol afforded the product (11.02 g; 63%) as yellow crystals, m.p. 151-153°C; $\nu_{max}$ 2220, 1519, and 1325 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 7.04-7.60 (9H, m), 8.12 (1H, s); (Found: C, 72.2; H, 4.1; N, 11.3%. $C_{15}H_{10}N_2O_2$ requires C, 72.0; H, 4.0; N, 11.2%). m/e 251 ($M^+$, 31%), 204 (100), 177 (9), 102 (11); $m^*$ 166.5 (250 -> 204), 153.6 (204 -> 177).

Nitroethenes prepared by this method are given in Table 1. 2-(2,6-Dichlorophenyl)-1-phenylnitroethene was prepared by Dr. R. A. North.

TABLE 1

2-Aryl-1-phenylnitroethenes




| Compound | $R^1$ | $R^2$ | Yield | m.p. | lit m.p. |
|---|---|---|---|---|---|
| A | H | H | 59% | 71-72°C | 73-74°C[193] |
| B | H | $CH_3O$ | 58% | 150-151°C | 153°C[193] |
| C | H | $CH_3$ | 49% | 75-77°C | 73-75.5°C[193] |
| D | H | Cl | 85% | 111-112°C | 113-114°C[193] |
| E | H | $NO_2$ | 82% | 156-157°C | 159.3-159.8°C[193] |
| F | H | CN | 63% | 151-153°C | - |
| G | $CH_3O$ | $CH_3O$ | 39% | 167-169°C | 165-166°C[137] |
| H | $CH_3$ | $CH_3$ | 62% | 114.5-115.5°C | 115-116°C[193] |

The configuration of all these nitroethenes is E-. This is shown by an analysis of their U.V. absorption spectra, which exhibit an absorption beyond 300 nm.[194] The U.V. spectra of some of these have already been reported.[195] Absorption maxima for the others are given in Table 2.

TABLE 2

U. V. absorption maxima of 2-aryl-1-phenylnitroethenes

| Compound [a] | $\lambda_{max}$ (nm) |
|---|---|
| B | 237, 348 |
| C | 233, 326 |
| D | 231, 316 |
| E | 218, 314 |
| F | 225, 298 |

a) Compounds lettered as in Table 1.

(s) α-Ethylstilbene was prepared by a Wittig reaction. A solution of sodium ethoxide was prepared from sodium (1.38 g; 0.06 mol) and absolute ethanol (30 ml). This was added dropwise over 15 min under nitrogen to a refluxing solution of benzyltriphenylphosphonium chloride (19.42 g; 0.05 mol) and propiophenone (6.71 g; 0.05 mol) in absolute ethanol (80 ml). The resultant orange solution was heated under reflux with stirring until tlc showed an insignificant amount of propiophenone remaining (ca 24 h). The sodium chloride was filtered off and the solvent removed under reduced pressure. The residue was chromatographed on alumina, eluting with petrol ether (40-60)/ether (100:10) and monitoring the elution by glc ($2\frac{1}{2}$% OVI; 200°C). α-Ethylstilbene (9.94 g; 96%) was obtained as a colourless oil which glc showed to be a mixture of the two isomers in a ratio of ca 55:45.

(t) 2-Ethyl-1,2-diphenyl-1-nitroethene was prepared by the following route. The method of Drefahl and Crahmer[196] was used to add acetyl nitrate across the double bond of α-ethylstilbene. To a solution of α-

ethylstilbene (8.71 g; 42 mmol) in acetic anhydride (43 ml) and glacial acetic acid (35 ml) was added concentrated nitric acid (8.71 g) with stirring, in an ice bath. The solution was stirred for 30 min in the ice bath and then for a further hour, allowing it to warm up to room temperature. It was then poured onto ice and the resultant yellow oil extracted with dichloromethane and dried. Removal of the solvent under reduced pressure yielded a yellow oil (13.65 g).

The crude oil was dissolved in dichloromethane (100 ml) and anhydrous sodium carbonate (21.2 g; 0.2 mol) added. The mixture was heated under reflux with rapid stirring for 24 h, the solid filtered off, and the solvent removed under reduced pressure leaving a yellow oil (11.0 g). This oil was chromatographed on alumina, eluting with petrol ether (40-60)/ether (100:20). A yellow oil (7.71 g) was obtained, and this partially crystallised on standing. The solid was filtered off and washed with hexane to give 2-ethyl-1,2-diphenyl-1-nitroethene (1.61 g; 15% based on α-ethylstilbene) as pale yellow crystals, m.p. 114.5-115.5°C from ethanol (89% recovery); $\nu_{max}$ 1520 ($NO_2$), 1360 $cm^{-1}$ ($NO_2$), $\delta_H$ ($CDCl_3$): 0.91 (3H, t, $J_{HH}$ = 7.5 Hz, $CH_3$), 2.39 (2H, q, $J_{HH}$ = 7.5 Hz, $CH_2$), 7.18-7.60 (10H, m, PhH); $\delta_C$ ($CDCl_3$): 148.7, 141.2, 136.6, 131.4, 129.7-127.1, 27.4, 12.2 p.p.m. (Found: C, 76.1; H, 6.1; N, 5.4%. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%). m/e 253 ($M^+$, 61%), 207 (37), 194 (33), 178 (41), 129 (100), 105 (35), 91 (63). The U.V. spectrum shows $\lambda_{max}$ 233 nm (ε 9900) indicating the compound has Z-stereochemistry (trans).

A sample of 2-(2-furyl)-1-phenylnitroethene was kindly provided by Professor J.I.G. Cadogan. Z-2-methyl-1,2-diphenyl-1-nitroethene was prepared by Dr. E. Abbot by the above route.

(u) 3-Ethyl-3-phenylphthalide was prepared by the method of Berti.[197] Ethyl magnesium iodide was prepared from magnesium (4.1 g; 0.169 mol) and ethyl iodide (26.5 g; 0.170 mol) in ether (120 ml) and reacted with o-benzoylbenzoic acid (12.9 g; 0.057 mol) in ether (100 ml). Work-up gave the required product (6.65 g; 49%) as a colourless oil, b.p. 164-166°C/0.5 mm (lit[197] 184-186°C/3 mm); $\delta_H$ ($CDCl_3$): 0.79 (3H, t, $J_{HH}$ = 8 Hz, $CH_3$), 2.38 (2H, m, $CH_2$), 7.22-7.75 (8H, m, ArH), 7.80-7.95 (1H, m, ArH); $\delta_C$ ($CDCl_3$): 169.8, 152.4, 140.1, 134.0, 128.8, 128.4, 127.8, 125.3, 124.7, 121.9, 90.1, 32.9, 7.7 p.p.m.

Reaction of the compound with hydroxylamine failed to give the oxime.

(v) 2-Bromoethylbenzene was prepared by the general method of Kamm and Marvel[198] by reaction of 2-phenylethanol (22 g, 0.18 mol) with 48% hydrobromic acid (80 g) and concentrated sulphuric acid (21 g). Work-up gave the product (15.8 g; 47%) as a colourless liquid, b.p. 82-83°C/7 mm (lit[199] 96.5-98.5°C/13 mm).

(w) Diphenyl-2-phenylethylphosphine oxide was prepared by a Michaelis-Arbusov reaction. A mixture of methyl diphenylphosphinite (2.16 g; 10 mmol) and 2-bromoethylbenzene (2.78 g; 15 mmol) in benzene (20 ml) was heated under reflux under nitrogen for 105 h. The solvent was removed under reduced pressure, the residue dissolved in ether, and the ether solution washed several times with water and dried. The ether was then removed under reduced pressure and the residue recrystallised from petrol (60-80) to give the product (0.42 g; 14%) as a white solid, m.p. 97-101°C (lit[200] 104-106°C); $\delta_P$ ($CDCl_3$): +31.6 p.p.m.

(x) Diphenyl-1-phenylethylphosphine oxide was prepared by a Michaelis-Arbusov reaction. A mixture of methyl diphenylphosphinite (2.16 g; 10 mmol) and 1-bromoethylbenzene (2.78 g; 15 mmol) in benzene (20 ml) was

heated under reflux under nitrogen for 92 h. A precipitate was formed on cooling the reaction mixture. The precipitate was filtered off, washed with water, and recrystallised from cyclohexane to give the product (1.00 g; 33%) as a white solid, m.p. 157-158°C (lit[201] 140-141°C, lit[202] 156-157°C for the (Sp)-(Sc)oxide); $\delta_P$ ($CDCl_3$): +33.7 p.p.m.

(y) Phenylacetaldoxime was prepared by the method of Dollfus.[203] Neutral hydroxylamine solution was prepared by reaction of hydroxylamine hydrochloride (6.95 g; 0.1 mol) in water (20 ml) with sodium carbonate decahydrate (14.31 g; 0.05 mol) in water (70 ml). This was reacted with a solution of phenylacetaldehyde (6.0 g; 0.05 mol) in ethanol (200 ml) at room temperature. Work-up followed by recrystallisation from ethanol and sublimation (95°C/0.04 mm) gave phenylacetaldoxime (2.35 g; 35%), m.p. 96.5-98°C (lit[203] 97-99°C); $\delta_C$ ($CDCl_3$): 150.8 (C=N), 136.6, 128.8, 126.7, 31.7 p.p.m.

(z) Phenylmethylhydroxamic Chloride was prepared by chlorination of phenylacetaldoxime. The oxime (2.03 g; 15 mmol) was dissolved in ether (50 ml) and cooled in an ice-salt bath. A 20% w/v solution of nitrosyl chloride in ether (10 ml; 2.0 g; 30 mmol) was added with stirring, producing an immediate green coloration. The mixture was stirred in the ice-salt bath for 30 min, and the solvent removed under reduced pressure at room temperature giving a green oil. Low temperature recrystallisation from chloroform/pentane gave the required product (0.56 g; 22%) as a white solid, m.p. 86.5-88.5°C (lit[204] 89-91°C); $\delta_C$ ($CDCl_3$): 141.9 (C=N), 134.3, 129.1, 128.7, 127.5, 42.8 p.p.m. m/e 171 ($M^+$).

(aa) Acetophenone Oxime. To a suspension of acetophenone (2.40 g; 20

mmol) in water (50 ml) was added a solution of hydroxylamine hydrochloride (2.78 g; 40 mmol) in water (20 ml) neutralised with a solution of sodium hydroxide (1.60 g; 40 mmol) in water (20 ml). The mixture was heated to its boiling point and just sufficient ethanol added to produce a clear solution. The solution was heated under reflux for a further 20 min, and then dry ice added. This resulted in the formation of a white precipitate which was filtered off, washed with water and dried. The precipitate was identified as the required product (1.20 g; 44%), m.p. 56-57°C (lit[205] 60°C); $\delta_C$ ($CDCl_3$): 156.0 (C=N), 136.5, 129.2, 128.5, 126.1, 12.4 p.p.m.

(ab) Benzaldoxime was prepared by essentially the same method as described in Vogel,[206] by reaction of a solution of hydroxylamine hydrochloride (45 g; 0.65 mol) in water (70 ml) with a mixture of the sodium bisulphite addition product of benzaldehyde (125 g; 0.60 mol) and a solution of sodium hydroxide (66 g, 1.65 mol) in water (160 ml). Work-up gave benzaldoxime (55.8 g; 77%) as a yellow oil; $\delta_C$ ($CDCl_3$): 150.5 (C=N), 131.9, 130.0, 128.7, 127.1 p.p.m.

(ac) Benzohydroxamic Chloride was prepared by the method of Perold, Steyn, and von Reiche.[207] Chlorine was passed through a suspension of benzaldoxime (27.0 g; 0.223 mol) in ca 8.3 M hydrochloric acid (180 ml) at 0°C. Work-up gave an orange oil which was recrystallised at low temperature from chloroform/pentane to give the required product (20.1 g; 58%) as an off-white solid, m.p. 46-48°C (lit[207] 42-48°C); $\delta_C$ ($CDCl_3$): 141.1 (C=N), 132.2, 130.9, 128.5, 127.2 p.p.m.

E. Deoxygenation of 2-Aryl-1-phenylnitroethenes

General method. A two-fold excess of triethyl phosphite was added to the 2-aryl-1-phenylnitroethene or to a solution of the 2-aryl-1-phenylnitroethene. The mixture was heated under reflux under nitrogen for 18 h, and the solvent and triethyl phosphite and phosphate then removed by distillation under reduced pressure. The residue was subjected to lplc on silica using petrol ether (40-60)/ether mixtures as the eluant.

(1) E-2-(4-Methoxyphenyl)-1-phenylnitroethene (a) The nitroethene (2.55 g; 10 mmol) was reacted with neat triethyl phosphite (7 ml; 40 mmol). Distillation gave a colourless distillate (5.44 g) and a brown oily residue (3.89 g) which was subjected to lplc. Elution with petrol/ether (100:40) gave an oily yellow solid (0.11 g) which was recrystallised from ethanol (11% recovery) to give a white solid identified as 2-(4-methoxyphenyl)-1-phenylethan-1-one (5%), m.p. 92-95°C (lit[208] 98-99°C); $\nu_{max}$ 1697 $cm^{-1}$ (C=O); $^1H$ n.m.r. as expected; m/e 226 ($M^+$, 45%), 121 ($CH_3OC_6H_4CH_2$, 100), 105 (PhCO, 87).

Further elution gave an off-white solid (0.15 g) which was recrystallised from ethanol (60% recovery) to give a white solid identified as 6-methoxy-2-phenylindole (7%), m.p. 174-175°C (lit[209] 176°C); $\nu_{max}$ 3400 $cm^{-1}$ (NH); $^1H$ n.m.r. as expected; m/e 223 ($M^+$).

Elution with petrol/ether (50:50) gave an unidentified green oil (0.11 g) and a fawn solid (0.31 g) identified as 6,6'-dimethoxy-2,2'-diphenyl-3,3'-biindolyl (14%), m.p. 225.5-227°C from ethanol (50% recovery); $\nu_{max}$ 3450 $cm^{-1}$ (NH); $\delta_H$ ($d_6$-DMSO): 3.75 (6H, s, $OCH_3$), 6.38-7.30 (12H, m, ArH), 7.37-7.60 (4H, m, ArH), 11.31 (2H, s, NH). (Found: C, 80.8;

H, 5.5; N, 6.1%. $(C_{15}H_{12}NO)_2$ requires C, 81.1; H, 5.4; N, 6.3%). m/e 444 ($M^+$, 100%), 429 (12), 414 (3), 222 (6), 214.5 (3), 207 (5); $m^*$ 414.5 (444 -> 429), 399.5 (429 -> 414).

(b) The nitroethene (2.55 g; 10 mmol) was reacted with triethyl phosphite (7 ml; 40 mmol) in 1, 2, 3-trichlorobenzene (25 g) at 212°C. The residue (6.32 g) after distillation was found by tlc to be a complex mixture of products. Elution with petrol/ether (100:25) gave an almost white crystalline solid (3.00 g) which was shown by tlc and I.R. to be residual 1, 2, 3-trichlorobenzene. Further elution with petrol/ether (100:25) gave the following fractions. (1) A brown oil (0.03 g) which was shown to be a mixture by glc (5% SE30; 158°C).

(2) A pale yellow solid (0.02 g) which was shown by tlc and I.R. to be 2-(4-methoxyphenyl)-1-phenylethan-1-one (1%); m/e 226.

(3) A brown oil (0.07 g) which was found to be a mixture by glc. I.R. and tlc showed that it contained 2-(4-methoxyphenyl)-1-phenylethan-1-one.

(4) A pale brown oily solid (0.05 g) which was found to be a mixture by glc.

Elution with petrol/ether (100:40) gave a light brown solid (0.11 g) which was shown by tlc and I.R. to be 6-methoxy-2-phenylindole (5%). Further elution gave a dark brown oil (0.08 g) which was a mixture by glc.

Elution with petrol/ether (50:50) gave a dark yellow crystalline solid (0.38 g) which was shown by I.R. and tlc to be 6, 6'-dimethoxy-2, 2'-diphenyl-3, 3'-biindolyl (17%).

(c) The nitroethene (2.55 g; 10 mmol) was reacted with triethyl phosphite (7 ml; 40 mmol) in dry benzene (20 ml). The residue (4.01 g) after

distillation was subjected to lplc. Elution with petrol/ether (100:40) gave a grey solid (0.027 g) which was shown by I.R. and tlc to be 6-methoxy-2-phenylindole (1.2%). Elution with petrol/ether (50:50) gave a brown oil (0.031 g) which was shown by tlc to be a complex mixture of products. Further elution with petrol/ether (50:50) gave a brown solid (0.31 g) which was shown by tlc and I.R. to be 6,6'-dimethoxy-2,2'-diphenyl-3,3'-biindolyl (14%).

(d) The nitroethene (2.55 g; 10 mmol) was reacted with triethyl phosphite (7 ml; 40 mmol) in the presence of added 6-methoxy-2-phenylindole (0.13 g). The residue (3.45 g) after distillation was chromatographed under low pressure.

Elution with petrol/ether (100:25) gave 2-(4-methoxyphenyl)-1-phenylethan-1-one (0.091 g; 4%) identified by its I.R. spectrum. Elution with petrol/ether (100:40) gave 6-methoxy-2-phenylindole (0.20 g; 9%) identified by its I.R. spectrum and by tlc. Elution with petrol/ether (50:50) gave 6,6'-dimethoxy-2,2'-diphenyl-3,3'-biindolyl (0.35 g; 16%) identified by tlc and by its I.R. spectrum.

(2) E-2-(4-Methylphenyl)-1-phenylnitroethene. The nitroethene (2.39 g; 10 mmol) was reacted with neat triethyl phosphite (7 ml; 40 mmol) and the residue (3.07 g) after distillation subjected to lplc.

Elution with petrol (40-60) gave an unidentified brown oily material (0.023 g) which had m/e 235.

Elution with petrol/ether (100:5) gave an oily solid (0.063 g) which was recrystallised from ethanol (16% recovery) and sublimed (150°C/10 mm; 60% recovery) to give a white solid (0.006 g) identified as 3,5-diphenyl-4-(4-methylphenyl)isoxazole, m.p. 198-199°C (lit[210] 198°C); $\delta_H(CDCl_3)$:

2.38 (3H, s), 7.10 (4H, s), 7.16-7.65 (10H, m); m/e 311 ($M^+$). Further elution with petrol/ether (100:5) gave an oily solid (0.093 g) which was purified by sublimation (100°C/10 mm; 48% recovery) giving 2-(4-methylphenyl)-1-phenylethan-1-one (4.4%) as a white solid, m.p. 95-96°C (lit[211] 95.5°C) from ethanol (76% recovery); $\nu_{max}$ 1687 $cm^{-1}$ (CO); $\delta_H$ ($CDCl_3$): 2.28 (3H, s, $CH_3$), 4.19 (2H, s, $CH_2$), 7.09 (4H, s, ArH), 7.26 - 7.62 (3H, m, PhH), 7.88-8.10 (2H, m, o-PhH); m/e 210 ($M^+$).

Elution with petrol/ether (100:10) gave a yellow-brown solid (0.31 g) identified as 6-methyl-2-phenylindole (15%), which was obtained as white crystals, m.p. 192-193°C from ethanol (52% recovery); $\nu_{max}$ 3445 $cm^{-1}$ (NH); $\delta_H$ ($d_6$-acetone): 2.38 (3H, s, $CH_3$), 6.72-6.90 (2H, m, ArH), 7.08-7.50 (5H, m, ArH), 7.68-7.88 (2H, m, ArH), 10.40 (1H, broad s, NH, not removed by $D_2O$ shake, but position shifted downfield). (Found: C, 86.7; H, 6.3; N, 6.7%. $C_{15}H_{13}N$ requires C, 86.9; H, 6.3; N, 6.8%). m/e 207 ($M^+$, 100%), 206 (44), 103.5 (6).

(3) E-2-(4-Chlorophenyl)-1-phenylnitroethene. The nitroethene (2.60 g; 10 mmol) was reacted with triethyl phosphite (7 ml; 40 mmol) and the deep red residue (3.67 g) remaining after distillation was chromatographed under low pressure.

Elution with petrol/ether (100:10) gave a brown oil (0.157 g) which was shown by glc (5% SE30; 154°C) to be a complex mixture of products. No attempt to separate the mixture was made. Further elution gave an oily brown solid (0.077 g) which was obtained as a white solid after recrystallisation from ethanol (31% recovery) and sublimation (106°C/0.2 mm; 81% recovery). This was identified as 2-(4-chlorophenyl)-1-phenylethan-

1-one (3.3%), m.p. 137-139°C (lit[211] 136.5°C); $\nu_{max}$ 1685 $cm^{-1}$ (CO); $\delta_H$ ($CDCl_3$): 4.24 (2H, s, $CH_2$), 7.10-7.62 (7H, m, ArH), 7.92-8.10 (2H, m, o-PhH); m/e 232, 230 ($M^+$).

Elution with petrol/ether (100:20) gave a brown solid (0.27 g) which gave off-white crystals on recrystallisation from ethanol (48% recovery). This product was identified as 6-chloro-2-phenylindole (12%), m.p. 185.5-187°C; $\nu_{max}$ 3440 $cm^{-1}$ (NH); $\delta_H$ ($d_6$-acetone): 6.83-7.10 (2H, m, ArH), 7.18-7.60 (5H, m, ArH), 7.72-7.92 (2H, m, ArH), 10.84 (1H, broad s, NH, removed by $D_2O$ shake). (Found: C, 73.7; H, 4.4; N, 6.2%. $C_{14}H_{10}ClN$ requires C, 73.8; H, 4.4; N, 6.1%). m/e 229 ($M^+$, 37%), 227 ($M^+$, 100), 201 (1.5), 199 (3), 192 (3.5), 191 (5), 165 (6), 114.5 (5), 113.5 (14); $m^*$ 162.4 (227 -> 192), 161.0 (229 -> 192).

F. Formation of 4, 5-Dihydro-2-oxo-1, 2, 5-oxazaphosph(v)oles

General method. The tervalent phosphorus reagent (25 mmol) was dissolved in tert-butanol (20 ml) and the 2-aryl-1-phenylnitroethene (10 mmol) added. The mixture was stirred at room temperature until all the nitroethene was consumed (tlc). In a number of cases, the product was formed as a precipitate which was filtered, washed with dry ether, and dried under vacuum. In those cases where the product did not precipitate, the solvent and excess phosphorus reagent were removed under vacuum (oil pump) at room temperature.

(1) 4, 5-Dihydro-5, 5, 5-trimethoxy-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

Reaction of E-2-(4-methoxyphenyl)-1-phenylnitroethene (2.55 g;

10 mmol), with trimethyl phosphite (3 ml; 25 mmol) in tert-butanol (20 ml) gave after 141 h a white precipitate (2.99 g; 79%), m.p. 114-115°C, decomp.; $\nu_{max}$ 1565-1590 (multiple line), 1516, 1262, 1093, 1076, 1041, 1035 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 3.63 (9H, d, $J_{PH}$ = 12 Hz, $(CH_3O)_3P$), 3.72 (3H, s, $CH_3O$), 4.61 (1H, d, $J_{PH}$ = 23 Hz, CH-P), 6.83 (2H, half an AB system, J = 9 Hz, ArH), 7.15-7.40 (5H, m, ArH), 7.89-8.04 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -36.4 p.p.m. (Found: C, 56.9; H, 5.8; N, 3.6%. $C_{18}H_{22}NO_6P$ requires C, 57.0; H, 5.8; N, 3.7%). $M^+$ not observed.

(2) 4, 5-Dihydro-5, 5, 5-trimethoxy-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole

E-2-(4-Methylphenyl)-1-phenylnitroethene (2.39 g; 10 mmol) reacted in 5 h with trimethyl phosphite (3 ml; 25 mmol) in tert-butanol (20 ml) to give a white precipitate of the required product (2.92 g; 80%), m.p. 99-101°C, decomp.; $\nu_{max}$ 1581, 1563, 1224, 1045-1093 $cm^{-1}$ (multiple line); $\delta_H$ ($CDCl_3$): 2.30 (3H, d, $J_{PH}$ = 3 Hz, $CH_3$) 3.64 (9H, d, $J_{PH}$ = 13 Hz, $(CH_3O)_3P$), 4.64 (1H, d, $J_{PH}$ = 25 Hz, CH-P), 7.00-7.40 (7H, m, ArH), 7.85-8.06 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -36.5 p.p.m. (Found: C, 59.6; H, 6.0; N, 3.6%. $C_{18}H_{22}NO_5P$ requires C, 59.5; H, 6.1; N, 3.8%). m/e 363 ($M^+$).

(3) 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5, 5-trimethoxy-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole

E-2-(4-Chlorophenyl)-1-phenylnitroethene (2.60 g; 10 mmol) reacted with trimethyl phosphite (3 ml; 25 mmol) in tert-butanol (20 ml) in 22 h giving a white precipitate of the required product (3.36 g; 88%), m.p. 109.5-110.5°C, decomp.; $\nu_{max}$ 1581, 1563, 1225, 1043-1093 $cm^{-1}$

(multiple line); $\delta_H$ ($CDCl_3$): 3.63 (9H, d, $J_{PH}$ = 13 Hz, $(CH_3O)_3P$), 4.65 (1H, d, $J_{PH}$ = 26 Hz, CH-P), 7.15-7.45 (7H, m, ArH), 7.80-8.00 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -37.2 p.p.m. (Found: C, 53.4; H, 5.0; N, 3.5%. $C_{17}H_{19}ClNO_5P$ requires C, 53.2; H, 5.0; N, 3.6%). m/e 385, 383 ($M^+$).

(4) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole

E-2-(4-Methoxyphenyl)-1-phenylnitroethene (2.55 g; 10 mmol) reacted with triethyl phosphite (4.35 ml; 25 mmol) in tert-butanol (20 ml) in 68 h giving a pale yellow solution. Removal of the solvent gave an oil which eventually crystallised on standing in the freezer with a little added hexane. It was then filtered, washed with hexane, and dried, giving the required product (3.63 g; 86%) as white crystals, m.p. 91-93°C, decomp.; $\nu_{max}$ 1580, 1564, 1257, 1030-1105 $cm^{-1}$ (multiple line); $\delta_H$ ($CDCl_3$): 1.13 (9H, t of d, collapses to t on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 2 Hz, $CH_3$), 3.70 (3H, s, $CH_3O$), 4.00 (6H, quintet, collapses to q on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 7 Hz, $CH_2$), 4.65 (1H, d, $J_{PH}$ = 25 Hz, CH-P), 6.82 (2H, half an AB system, J = 8 Hz, ArH), 7.10-7.42 (5H, m, ArH), 7.85-8.08 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -37.3 p.p.m. (Found: C, 59.8; H, 6.7; N, 3.3%. $C_{21}H_{28}NO_6P$ requires C, 59.8; H, 6.7; N, 3.3%). m/e 421 ($M^+$).

(5) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

E-2-(4-Methylphenyl)-1-phenylnitroethene (2.39 g; 10 mmol) reacted with triethyl phosphite (4.35 ml; 25 mmol) in tert-butanol (20 ml) in 4 h giving an almost colourless solution. After removal of the solvent, the

resultant oil was diluted with a little hexane. After several days in the freezer, the oil crystallised and was filtered, washed with hexane and dried giving the phosph(v)ole (3.24 g; 80%) as white crystals, m.p. 46-48°C; $\nu_{max}$ 1580, 1567, 1050 $cm^{-1}$ (broad band); $\delta_H$ ($CDCl_3$): 1.12 (9H, t of d, collapses to t on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 2 Hz, $CH_3$), 2.29 (3H, d, $J_{PH}$ = 3 Hz, $CH_3$), 3.99 (6H, quintet, collapses to q on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 7 Hz, $CH_2$), 4.65 (1H, d, $J_{PH}$ = 25 Hz, CH-P), 6.96-7.40 (7H, m, ArH), 7.82-8.05 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -37.6 p.p.m. (Found: C, 62.1; H, 7.1; N, 3.4%. $C_{21}H_{28}NO_5P$ requires C, 62.2; H, 7.0; N, 3.4%). m/e 405 ($M^+$).

(6) 4-(4-Chlorophenyl)-5, 5, 5-triethoxy-4, 5-dihydro-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

E-2-(4-Chlorophenyl)-1-phenylnitroethene (2.60 g; 10 mmol) reacted with triethyl phosphite (4.35 ml; 25 mmol) in tert-butanol (20 ml) over a period of 22 h to give a pale yellow solution. Removal of the solvent gave an oil which was triturated with hexane to yield the product (2.01 g; 47%) as a white solid, m.p. 87-88.5°C; $\nu_{max}$ 1582, 1562, 1060 $cm^{-1}$ (broad band); $\delta_H$ ($CDCl_3$): 1.13 (9H, t of d, collapses to t on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 2 Hz, $CH_3$), 3.99 (6H, quin tet, collapses to q on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 7 Hz, $CH_2$), 4.67 (1H, d, $J_{PH}$ = 25 Hz, CH-P), 7.10-7.44 (7H, m, ArH), 7.84-8.02 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -38.4 p.p.m. (Found: C, 56.6; H, 5.9; N, 3.2%. $C_{20}H_{25}ClNO_5P$ requires C, 56.4; H, 5.9; N, 3.3%). m/e 427, 425 ($M^+$).

(7) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole

E-2-(2, 4, 6-Trimethoxyphenyl)-1-phenylnitroethene (3.15 g; 10 mmol) reacted with triethyl phosphite (4.35 ml; 25 mmol) in tert-butanol (20 ml) in 102 h to give the required product (4.07 g; 85%) as a white precipitate, m.p. 118.5-120.5°C, decomp.; $\nu_{max}$ 1583 (multiple line), 1107, 1085, 1055, 1037 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 1.13 (9H, t of d, collapses to t on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 1.5 Hz, $CH_3$), 3.71 (3H, s, p-$CH_3O$), 3.80 (6H, broad s, o-$CH_3O$), 4.02 (6H, quintet, collapses to q on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 7 Hz, $CH_2$), 5.45 (1H, d, $J_{PH}$ = 27 Hz, CH-P), 6.04 (2H, broad s, m-ArH), 7.06-7.33 (3H, m, PhH), 7.85-8.10 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -41.1 p.p.m. (Found: C, 57.4; H, 6.6; N, 2.8%. $C_{23}H_{32}NO_8P$ requires C, 57.4; H, 6.7; N, 2.9%). m/e 481 ($M^+$).

(8) 4-(2, 6-Dichlorophenyl)-5, 5, 5-triethoxy-4, 5-dihydro-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

E-2-(2, 6-Dichlorophenyl)-1-phenylnitroethene (2.94 g; 10 mmol) reacted with triethyl phosphite (4.35 ml; 25 mmol) in tert-butanol (20 ml) over a period of 47 h giving the phosph(v)ole (4.21 g; 91%) as a white precipitate, m.p. 109-110°C, decomp.; $\nu_{max}$ 1584, 1518, 1105, 1086, 1079, 1047 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 1.13 (9H, t of d, collapses to t on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 1.5Hz, $CH_3$), 4.06 (6H, quintet, collapses to q on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 7 Hz, $CH_2$), 5.83 (1H, d, $J_{PH}$ = 30 Hz, CH-P), 6.92-7.38 (6H, m, ArH), 7.85 (2H, d of d, $J_{HH}^3$ = 8 Hz, $J_{HH}^4$ = 2 Hz, o-PhH); $\delta_P$ ($CDCl_3$): -44.9 p.p.m. (Found: C, 52.0; H, 5.2; N, 2.9%. $C_{20}H_{24}Cl_2NO_5P$ requires C, 52.2; H, 5.3; N, 3.0%). m/e 463, 461, 459

($M^+$).

(9) 4, 5-Dihydro-5, 5-dimethoxy-4-(4-methoxyphenyl)-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole.

E-2-(4-Methoxyphenyl)-1-phenylnitroethene (1.28 g; 5 mmol) reacted with dimethyl phenylphosphonite (2.13 g; 12.5 mmol) in tert-butanol (10 ml) in 4 h to give the required product (2.07 g; 97%) as a white precipitate, m.p. 117.5-118°C; $\nu_{max}$ 1556, 1512, 1262, 1113, 1078, 1037 $cm^{-1}$; $^1H$ n.m.r. broad at room temperature due to coalescence (see later); $\delta_P$ ($CDCl_3$) (-30°C): -26.0, -18.4 p.p.m. (ratio ca 2:1). (Found: C, 64.7; H, 5.7; N, 3.2%. $C_{23}H_{24}NO_5P$ requires C, 64.9; H, 5.7; N, 3.3%). $M^+$ not observed.

(10) 4, 5-Dihydro-5, 5-dimethoxy-4-(4-methylphenyl)-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole.

E-2-(4-Methylphenyl)-1-phenylnitroethene (1.20 g; 5 mmol) reacted with dimethyl phenylphosphonite (2.13 g; 12.5 mmol) in tert-butanol (10 ml) in 20 min to give the phosph(v)ole (2.01 g; 98%) as a white precipitate, m.p. 127.5-128°C; $\nu_{max}$ 1578, 1557, 1227, 1116, 1082, 1039 $cm^{-1}$; $^1H$ n.m.r. broad at room temperature; $\delta_P$ ($CDCl_3$) (-30°C): -26.1, -18.5 p.p.m. (ratio ca 3:2). (Found: C, 67.2; H, 6.0; N, 3.3%. $C_{23}H_{24}NO_4P$ requires C, 67.5; H, 5.9; N, 3.4%). $M^+$ not observed.

(11) 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5-dimethoxy-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole.

E-2-(4-Chlorophenyl)-1-phenylnitroethene (2.60 g; 10 mmol) reacted with dimethyl phenylphosphonite (4.26 g; 25 mmol) in tert-butanol (20 ml) in 2 h to give the required product (4.30 g; 100%) as a white precipitate,

m.p. 125°C, decomp.; $\nu_{max}$ 1580, 1556, 1225, 1113, 1078, 1026 $cm^{-1}$; $^1H$ n.m.r. broad at room temperature; $\delta_P$ ($CDCl_3$) (-28°C): -26.8, -19.2 p.p.m. (ratio ca 5:2). (Found: C, 61.3; H, 5.0; N, 3.1%. $C_{22}H_{21}ClNO_4P$ requires C, 61.5; H, 4.9; N, 3.3%). $M^+$ not observed.

(12) Attempted oxazaphosph(v)ole formation from E-2-(4-nitrophenyl)-1-phenylnitroethene.

(a) E-2-(4-Nitrophenyl)-1-phenylnitroethene (2.70 g; 10 mmol) reacted with trimethyl phosphite (3 ml; 25 mmol) in tert-butanol (20 ml) over a period of 20 h to give an orange solution and a yellow precipitate. The precipitate was filtered off and washed three times with ether. I.R. showed it to be unreacted nitroethene (0.53 g; 20% recovery). The solvent was removed from the filtrate leaving an orange oil. All attempts to crystallise the oil failed, and subsequent $^{31}P$ n.m.r. showed it to be only a complex mixture of P=O compounds. No phosph(v)ole was observed.

(b) The nitroethene (2.70 g; 10 mmol) reacted with triethyl phosphite (4.35 ml; 25 mmol) in tert-butanol (20 ml) in 19 h to give a deep red solution, which was shown by tlc to be a complex mixture of products. $^{31}P$ N.m.r. showed large peaks due to triethyl phosphite and triethyl phosphate, smaller peaks at +16.4 and +13.5 p.p.m., and smaller peaks yet at -8.2 and -28.6 p.p.m.

(13) Attempted oxazaphosph(v)ole formation from E-2-(4-cyanophenyl)-1-phenylnitroethene.

(a) E-2-(4-Cyanophenyl)-1-phenylnitroethene (2.50 g; 10 mmol) was reacted with triethyl phosphite (4.35 ml; 25 mmol) in tert-butanol (20 ml) for 43 h. Tlc showed the presence of unreacted nitroethene, and the $^{31}P$

n. m. r. spectrum exhibited significant peaks due to triethyl phosphite and triethyl phosphate, and at +31. 9 and +17. 0 p. p. m., but only a small peak at -28. 2 p. p. m.

(b) Two reactions were carried out on an n. m. r. tube scale. The nitroethene (0. 050 g; 0. 2 mmol) was added to a solution of triethyl phosphite (50 μl) in the alcohol (ca 0. 4 ml), and the tubes shaken for 19 h on a mechanical shaker. They were then examined by $^{31}P$ n. m. r.

(i) With tert-butanol as the solvent, some of the nitroethene remained unreacted, and $^{31}P$ n. m. r. showed the presence of triethyl phosphite, triethyl phosphate and three other compounds with shifts in the P=O region. Only a tiny peak at -28. 3 p. p. m. was evident in the phosphorane region.

(ii) In ethanol, some of the nitro compound remained unreacted, and $^{31}P$ n. m. r. showed no phosphite, but indicated the presence of a large amount of triethyl phosphate plus another seven compounds with shifts in the P=O region. No peak was visible in the phosphorane region of the spectrum.

(14) Other oxazaphosph(v)oles which were prepared were 5, 5, 5-triethoxy-4, 5-dihydro-2-oxo-3, 4-diphenyl-1, 2, 5-oxazaphosph(v)ole (29%), m. p. 72-74°C (lit[137] 63-65°C), and 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole (42%), m. p. 85-88°C, decomp. (lit[137] 80-83°C).

G. High Temperature Deoxygenation of 4, 5-Dihydro-2-oxo-1, 2, 5-oxazaphosph(v)oles.

(1) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

(a) A solution of the phosph(v)ole (1.01 g; 2.5 mmol) in triethyl phosphite (5 ml) was added dropwise over a period of several hours to refluxing triethyl phosphite (10 ml) under nitrogen. The mixture was refluxed for a total of 18 h giving an orange solution. The solvent was removed by Kugelrohr distillation (90°C/0.1 mm) and the residue (0.83 g) subjected to lplc on silica.

Elution with petrol/ether (100:5) gave an unidentified orange solid (0.015 g) which had m/e 323. Elution with petrol/ether (100:10) gave 6-methyl-2-phenylindole (0.062 g; 12%) as an off-white solid, m.p. 189-190.5°C from ethanol (47% recovery); I.R. and $^{1}$H n.m.r. identical to those obtained previously.

(b) The phosph(v)ole (1.01 g; 2.5 mmol) was dissolved in triethyl phosphite (5 ml) and the solution heated under reflux under nitrogen for 18 h. After removal of the solvent, a yellow oil (1.35 g) was obtained, and this was chromatographed on silica under low pressure.

Elution with petrol/ether (100:5) gave an unidentified orange oily solid (0.006 g). Elution with petrol/ether (100:10) gave a pale yellow solid (0.029 g) which was recrystallised from ethanol (59% recovery) to give an off-white solid identified by its I.R. spectrum as 6-methyl-2-phenylindole (5.6%), m.p. 189-191°C.

(2) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

A solution of the phosph(v)ole (1.05 g; 2.5 mmol) in triethyl phosphite (6 ml) was added dropwise over several hours to refluxing triethyl phosphite (9 ml) under nitrogen. The solution was heated under reflux for a total of 18 h, after which the triethyl phosphite was removed leaving a yellow-brown oily residue (1.42 g). This was subjected to lplc on silica.

Elution with petrol/ether (100:25) gave 6-methoxy-2-phenylindole (0.099 g; 18%) as a fawn solid, m.p. 174-175°C (lit[209] 176°C) from ethanol (52% recovery); I.R. identical to that obtained previously. Elution with petrol/ether (50:50) gave a solution which was shown by tlc to contain 6, 6'-dimethoxy-2, 2'-diphenyl-3, 3'-biindolyl, but evaporation of the solvent gave no measurable amount of product.

(3) Deoxygenation of 4-(4-chlorophenyl)-5, 5, 5-triethoxy-4, 5-dihydro-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

The phosph(v)ole (1.06 g; 2.5 mmol) was dissolved in triethyl phosphite (5 ml) and the solution added dropwise over several hours to refluxing triethyl phosphite (10 ml) under nitrogen. The solution was heated under reflux for a total of 18 h giving an orange solution. Removal of the phosphite gave an orange oily residue (1.36 g), which was subjected to lplc on silica.

Elution with petrol/ether (100:10) gave the following fractions.

(a) An unidentified brown oil (0.009 g).

(b) Another unidentified brown oil (0.009 g).

(c) A yellow-brown solid (0.047 g) which was recrystallised from

ethanol (47% recovery) to give an off-white solid. This was shown by tlc, I.R., and $^{1}$H n.m.r. to be a mixture of 6-chloro-2-phenylindole and 2-(4-chlorophenyl)-1-phenylethan-1-one. $^{1}$H N.m.r. showed the aromatic integral to be 154 units and the ketone methylene group integral to be 4 units. From this, it can be calculated that the proportion of indole to ketone is 8:1. The reaction product is therefore an 8:1 mixture of 6-chloro-2-phenylindole (7.3%) and 2-(4-chlorophenyl)-1-phenylethan-1-one (0.9%).

(4) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-2-oxo-3, 4-diphenyl-1, 2, 5-oxazaphosph(v)ole.

A solution of the phosph(v)ole (0.98 g; 2.5 mmol) in triethyl phosphite (5 ml) was added dropwise over several hours to refluxing triethyl phosphite (10 ml) under nitrogen. The mixture was refluxed for a total of 18 h giving an orange solution. Removal of the solvent gave a brown residue (0.97 g) which was chromatographed on silica under low pressure.

Elution with petrol/ether (100:5) gave the following fractions.

(a) An unidentified greenish-brown oil (0.011 g).

(b) An unidentified reddish-brown oil (0.032 g).

(c) A yellow-brown solid (0.056 g) which was recrystallised from ethanol (38% recovery) to give yellow crystals, which were identified by tlc and I.R. as 2-phenylindole (12%), m.p. 187-188.5°C (lit[205] 189°C).

(5) Deoxygenation of 4-(2, 6-dichlorophenyl)-5, 5, 5-triethoxy-4, 5-dihydro-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

A mixture of the phosph(v)ole (1.15 g; 2.5 mmol) and triethyl phosphite (4 ml) was heated for 15 min at 148°C under nitrogen. Excess phosphite was pumped off at room temperature and the resultant orange-brown oily

residue (1.73 g) chromatographed on silica under low pressure.

Elution with petrol/ether (100:10) gave an orange oil (0.147 g) which was recrystallised from cyclohexane (41% recovery) to give a fawn solid (0.060 g). Sublimation (65°C/0.01 mm) of this solid gave 2-(2,6-dichlorophenyl)-3-phenyl-2H-azirine (0.041 g; 6.3%) as a white sublimate, m.p. 85°C; $\nu_{max}$ ($CHCl_3$) 1741 (C=N), 1560, 1451, 1441, 1435 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 3.53 (1H, s), 6.94-7.33 (3H, m, ArH), 7.45-7.66 (3H, m, ArH), 7.87-8.10 (2H, m, o-PhH). (Found: C, 64.3; H, 3.5; N, 5.3%. $C_{14}H_9Cl_2N$ requires C, 64.1; H, 3.5; N, 5.3%). m/e 265 ($M^+$, 11%), 263 ($M^+$, 58), 261 ($M^+$, 87), 228 (15), 226 (42), 191 (16), 162 (4), 160 (21), 158 (32), 125 (35), 123 (100); $m^*$ 195.7 (261 -> 226), 161.4 (226 -> 191), 95.7 (261 -> 158 or 158 -> 123).

Elution with petrol/ether (100:25) gave an unidentified yellow-brown oily solid (0.021 g).

Elution with petrol/ether (50:50) gave a yellow solid (0.137 g) which was recrystallised from ethanol (83% recovery) to give colourless crystals identified as a mixture of two isomers of diethyl 1,5-di-(2,6-dichlorophenyl)-2-phenyl-4-phenylimino-3-azapent-1-ene-1-phosphonate (17%) plus half a mole of ethanol of recrystallisation, m.p. 133-134°C and 154-157°C; $\nu_{max}$ 3360 (broad) (NH), 1664 (C=N), 1592, 1491, 1240 (P=O), 1225, 1069 (POC), 1030 (POC), 749 $cm^{-1}$ (C-Cl); $\nu_{max}$ ($CHCl_3$) 3670 (OH), 3380 $cm^{-1}$ (NH); $\delta_H$ ($CDCl_3$): 1.22 (ca 7H, t, $J_{HH}$ = 7 Hz, $CH_3$), 1.85 (0.5H, s, OH), 3.70 (1H, q, $J_{HH}$ = 7 Hz, collapses to s on irradiation at 1.2δ, $CH_2$), 3.83 (2H, s, $CH_2$), 4.00-4.45 (4H, m, simplified slightly on irradiation at the phosphorus frequency, $CH_2$), 6.48-7.26 (ca 17H, m, ArH + NH), $\delta_P$ ($CDCl_3$): +13.7 p.p.m.; $\delta_C$ ($CDCl_3$): 151.5, 148.5, 142.3, 136.0, 135.6,

132.6, 130.0-126.8, 121.7, 120.5, 62.7 (d, $J_{PC}$ = 5.7 Hz), 33.7, 16.2 p.p.m. (d, $J_{PC}$ = 7.3 Hz). (Found: C, 57.8; H, 4.5; N, 4.0%. $C_{32}H_{29}Cl_4N_2O_3P.CH_3O_{0.5}$ requires C, 57.8; H, 4.7; N, 4.1%). The compound gives two identical mass spectra, one at a higher probe temperature than the other. m/e 662 ($M^+$ +2, 6%), 660 ($M^+$, 5) (the parent ion exhibits a four chlorine pattern), 514 (34) (two chlorine pattern), 262 (54) (two chlorine pattern), 159 (100) (two chlorine pattern), 77 (58); $m^*$ ca 401 ($M^+$ -> 514), 96.5 (262 -> 159).

H. N.M.R. Investigation of Deoxygenation of 4, 5-Dihydro-2-oxo-1, 2, 5-oxazaphosph(v)oles

(1) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

(a) The phosph(v)ole (0.0843 g; 0.2 mmol) was dissolved in $d_6$-benzene (0.3 ml) in an n.m.r. tube filled with nitrogen and triethyl phosphite (36 µl; slight excess) added. The reaction was followed at 72°C by $^{31}P$ n.m.r. After 10 min, a peak due to triethyl phosphate had appeared. After 45 min, the phosphate peak had increased relative to the phosphite and the original phosph(v)ole, and a new peak had appeared at -27.6 p.p.m. After 70 min, a new peak appeared at +18.6 p.p.m. After 90 min, the phosphate had again increased relative to the phosphite, and the peak at -27.6 p.p.m. had increased relative to the original phosph(v)ole. After a further 6 h, no peaks remained in the phosphorane region, but there was a large peak due to triethyl phosphate and smaller peaks due to triethyl phosphite and at +18.9 and +20.3 p.p.m.

(b) The same reaction was carried out, this time at 60°C. After 4 h, the $^{31}P$ n.m.r. spectrum showed the presence of triethyl phosphate and the compound at -27.6 p.p.m., both peaks being of roughly equal intensity. After 5 h, the phosphate peak had increased relative to the peak at -27.6 p.p.m. After 12 h, the peak at -27.6 p.p.m. had increased relative to the original phosph(v)ole peak, but the phosphate peak had increased relative to both of these. Other products were becoming significant. After 28 h, there was a very large phosphate peak plus other significant peaks, particularly at +18.9 and +20.3 p.p.m. There was still a small amount of the original phosph(v)ole remaining, but there was no longer a peak at -27.6 p.p.m.

(c) The phosph(v)ole (0.21 g; 0.5 mmol) and methyl diphenylphosphinite (0.5 ml; excess) were mixed and left to stand under nitrogen at room temperature for 15 h. Subsequent $^{31}P$ n.m.r. showed the phosph(v)ole to be unchanged. The mixture was then heated at 60-65°C. After 3.5 h, a significant amount of the original phosph(v)ole remained, and there were smaller peaks due to triethyl phosphate and methyl diphenylphosphinate, and at -29.3 p.p.m. After 7 h, there were peaks due to (in order of decreasing size) methyl diphenylphosphinate, triethyl phosphate, the compound at -29.3 p.p.m., and the original phosph(v)ole, in addition to other smaller peaks. After 16 h, there was no peak due to the original phosph(v)ole and only a small peak at -29.3 p.p.m. There were large peaks due to triethyl phosphate and methyl diphenylphosphinate, a significant peak at +13.9 p.p.m., plus other smaller peaks.

(2) <u>Deoxygenation of 4-(4-chlorophenyl)-5, 5, 5-triethoxy-4, 5-dihydro-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.</u>

The phosph(v)ole (0.085 g; 0.2 mmol) and triethyl phosphite (ca 0.4 ml) were heated under nitrogen in an n.m.r. tube at 118°C. After 30s, $^{31}$P n.m.r. showed peaks due to triethyl phosphite, triethyl phosphate, equal intensity peaks due to the original phosph(v)ole and a compound at -28.1 p.p.m., plus small peaks in the P=O region. After 60s, there was only a small peak due to the original phosph(v)ole. After 90s, there were only peaks due to phosphite, phosphate, and the compound at -28.1 p.p.m., in addition to small peaks in the P=O region.

(3) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

The phosph(v)ole (0.081 g; 0.2 mmol) was reacted with triethyl phosphite (ca 0.3 ml) under nitrogen in an n.m.r. tube at 122°C. After 2 min, $^{31}$P n.m.r. showed large peaks due to triethyl phosphite, triethyl phosphate, and a compound at -27.8 p.p.m. There were also several small peaks in the P=O region and a very tiny peak due to the original phosph(v)ole.

(4) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

A mixture of the phosph(v)ole (0.096 g; 0.2 mmol) and triethyl phosphite (ca 0.3 ml) was heated in an n.m.r. tube under nitrogen at 150°C. After 20s, $^{31}$P n.m.r. showed large peaks due to triethyl phosphite, triethyl phosphate, and a compound at -26.2 p.p.m., and a small peak due to the original phosph(v)ole. After 1 min, none of the original phosph(v)ole remained and there were peaks due to phosphite, phosphate and the compound at -26.2 p.p.m.

(5) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

The phosph(v)ole (0.087 g; 0.2 mmol) was dissolved in triethyl phosphite (ca 0.3 ml) in an n.m.r. tube under nitrogen, and the solution heated at 154°C. After 30s, $^{31}$P n.m.r. showed only triethyl phosphite, triethyl phosphate, and a compound at -26.8 p.p.m.

(I) Formation of 4, 5-Dihydro-1, 2, 5-oxazaphosph(v)oles.

(1) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

A mixture of 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole (2.41 g; 5 mmol) and triethyl phosphite (10 ml; excess) was heated under nitrogen at 150°C for 1 min, giving a yellow solution. $^{31}$P N.m.r. of the solution showed only triethyl phosphite, triethyl phosphate, and the expected product (-26.1 p.p.m.). The phosphate and excess phosphite were pumped off at room temperature leaving a mass of yellow crystals. A small quantity of yellow supernatant liquid was decanted off and the crystals washed with hexane and then ether, giving the required product (1.16 g; 50%) as a nearly white solid, m.p. 101-103°C; $\nu_{max}$ 1609, 1598, 1114, 1060 cm$^{-1}$; $\delta_H$ ($CDCl_3$): 1.09 (9H, t of d, collapses to t on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 1.5 Hz, $CH_3$), 3.57 (3H, broad s, o-$OCH_3$), 3.68 (3H, s, p-$OCH_3$), 3.89 (3H, broad s, o-$OCH_3$), 3.92 (6H, m, collapses to q on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 6 Hz, $CH_2$), 4.68 (1H, d,

$J_{PH}$ = 23.5 Hz, CH-P), 5.92 (1H, broad s, m-ArH), 6.11 (1H, broad s, m-ArH), 7.10-7.30 (3H, m, PhH), 7.44-7.68 (2H, d of d, $J_{HH}^{3}$ = 7 Hz, $J_{HH}^{4}$ = 3 Hz, o-PhH); $\delta_P$ ($CDCl_3$): -26.0 p.p.m. (Found: C, 59.1; H, 6.8; N, 2.9%. $C_{23}H_{32}NO_7P$ requires C, 59.3; H, 6.9; N, 3.0%). m/e 465 ($M^+$, 0.3%), 419 (100), 390 (12), 282 (41), 179 (29); $m^*$ 189.8 (419 -> 282), 363.0 (419 -> 390).

(2) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethylphenyl)-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

A mixture of 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole (4.34 g; 10 mmol) and triethyl phosphite (12 ml) was heated under nitrogen in an oil bath at 162°C for 90s with rapid stirring. The solution was then cooled in an ice bath. $^{31}P$ N.m.r. of the solution showed only triethyl phosphite, triethyl phosphate, and the expected product. The phosphate and excess phosphite were pumped off at room temperature leaving an oil which was triturated twice with water to remove residual phosphate, extracted with ether, and dried. The ether was then removed under reduced pressure and the resultant oil diluted with a little hexane. After several days in the freezer, colourless crystals were formed, and these were filtered off, washed with hexane, and dried, giving the required phosph(v)ole (1.74 g; 42%), m.p. 61-63°C; $\nu_{max}$ 1109, 1082, 1051 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 1.13 (9H, broad t, sharpened on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $CH_3$), 2.07 (3H, d, $J_{PH}$ = 1.5 Hz, $CH_3$), 2.16 (3H, d, $J_{PH}$ = 2 Hz, $CH_3$), 2.55 (3H, broad s, sharpened on irradiation at the phosphorus frequency, $CH_3$), 3.76-4.25 (6H, m, simplified on irradiation at the phosphorus frequency, $CH_2$), 4.32 (1H, d, $J_{PH}$ = 27 Hz, CH-P), 6.59 (1H, broad s, m-ArH), 6.83 (1H, broad s, m-ArH), 7.08-

7.28 (3H, m, PhH), 7.35-7.56 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): -26.3 p.p.m. (Found: C, 66.1; H, 7.6; N, 3.3%. $C_{23}H_{32}NO_4P$ requires C, 66.2; H, 7.7; N, 3.3%). m/e 417 ($M^+$, 0.4%), 371 (100), 234 (60).

(3) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(4-methylphenyl)-3-phenyl-1, 2, 5-oxazaphosph(v)ole

A solution of 5, 5, 5-triethoxy-4, 5-dihydro-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole (3.45 g; 8.5 mmol) in triethyl phosphite (12.5 ml) was heated under nitrogen in an oil bath at 124°C for 2.5 min with stirring. $^{31}P$ N.m.r. of the solution showed a large peak due to triethyl phosphate, and a smaller than expected peak for the product, in addition to several small peaks in the P=O region. The solvent was pumped off at room temperature and the resultant yellow oil diluted with hexane. After a few days in the freezer, the oil crystallised. The crystals were filtered off, washed with hexane, and dried, giving a white solid (0.62 g) which was shown by $^{31}P$ n.m.r. to be an approximately 80% pure sample of the desired product ( $\delta_P$ ($CDCl_3$): -27.3 p.p.m.) contaminated with several compounds exhibiting chemical shifts in the P=O region.

J. Thermolysis of 1, 2, 5-Oxazaphosph(v)oles

(1) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

(a) The phosph(v)ole (0.078 g; 0.168 mmol) was subjected to flash vacuum pyrolysis at a pressure of $2 \times 10^{-3}$ mm and a furnace temperature of 500°C. The oven temperature was 70-80°C for the first 15 min, then 133°C for 2 h.

The phosphorane did not distil cleanly and a residue remained at the end of the experiment. $^{31}P$ N. m. r. ($CDCl_3$) of the residue showed peaks at +26. 2 (5902%), +23. 1 (2572%) and -3. 0 p. p. m. (1038%). A dark brown oily pyrolysate and a clear liquid pyrolysate were obtained. The dark brown oil exhibited the following $\delta_P$ ($CDCl_3$): + 29. 1 (1901%), +22. 2 (6478%), +21. 8 (1305%), +21. 0 (10345%) and -2. 1 p. p. m. (1412%). The clear liquid was shown to be triethyl phosphate by $^1H$ and $^{31}P$ n. m. r. Addition of cyclohexane (5 µl) as an n. m. r. calibrant gave the yield as 0. 101 mmol (60%).

(b) The phosph(v)ole (1. 16 g; 2. 5 mmol) was thermally decomposed in a Kugelrohr bulb distillation apparatus. After 2 h at 120°C/0. 01 mm, there was obtained a distillate (0. 03 g) which was shown by $^1H$ and $^{31}P$ n. m. r. to be triethyl phosphate. $^{31}P$ N. m. r. of the yellow oily residue showed most of the phosphorane to be unchanged. Some of the phosphorane still remained unchanged after a further 2. 5 h at 143°C/0. 01 mm. After a further 2 h at 150°C, all the phosphorane had decomposed and the residue was found to contain four main phosphorus-containing products. The liquid distillate (0. 15 g) was shown to be triethyl phosphate (33%) by $^1H$ and $^{31}P$ n. m. r. A yellow oily distillate (0. 042 g) was also obtained but this was found to be a mixture by tlc. Preparative tlc did not afford any significant amounts of products.

(c) A solution of the phosph(v)ole (2. 33 g; 5 mmol) in t-butylbenzene (20 ml) was added dropwise over a period of 2 h to refluxing t-butylbenzene (10 ml) under nitrogen. The solution was then heated under reflux for a further hour, giving a fluorescent deep orange solution. $^{31}P$ N. m. r. of

the solution showed only one peak, due to triethyl phosphate. The solvent was removed under reduced pressure, leaving a brown oil (3.02 g) which was chromatographed on silica under low pressure.

Elution with petrol/ether (100:25) gave a pale yellow liquid (0.82 g) which was shown by $^{1}$H n.m.r. to be a mixture of t-butylbenzene and petrol residues. Elution with petrol/ether (50:50) gave a fawn solid (0.112 g) which was recrystallised from ethanol (74% recovery) to give a white fibrous solid identified as N-phenyl-2-(2,4,6-trimethoxyphenyl)acetamide (7.4%), m.p. 132.5-133.5°C; $\nu_{max}$ 3300 (NH), 1665 cm$^{-1}$ (CO); $\delta_H$ ($CDCl_3$): 3.67 (2H, s, $CH_2$), 3.77 (3H, s, p-$OCH_3$), 3.78 (6H, s, o-$OCH_3$), 6.14 (2H, s, m-ArH), 6.87-7.50 (5H, m, PhH), 7.68 (1H, broad s, NH). (Found: C, 67.8; H, 6.3; N, 4.6%. $C_{17}H_{19}NO_4$ requires C, 67.8; H, 6.4; N, 4.6%). m/e 301 ($M^+$, 38%), 208 (ArCHCO, 14), 181 ($ArCH_2$, 100), 136 ($(CH_3O)_2C_6H_2$, 17), 121 (14), 120 (PhNHCO, 15), 92 (PhNH, 15). Further elution gave a yellow-brown solid (0.159 g) which was shown to be a mixture by tlc. Recrystallisation from ethanol gave an off-white solid (0.024 g) which was shown by tlc and I.R. to be N-phenyl-2-(2,4,6-trimethoxyphenyl)acetamide (1.6%), m.p. 130-131°C

(2) 5,5,5-Triethoxy-4,5-dihydro-4-(2,4,6-trimethylphenyl)-3-phenyl-1,2,5-oxazaphosph(v)ole.

A solution of the phosph(v)ole (1.54 g; 3.7 mmol) in t-butylbenzene (20 ml) was added dropwise over a period of 25 min to refluxing t-butylbenzene (10 ml) under nitrogen. The solution was heated under reflux for a further 5 min giving a yellow solution. $^{31}$P N.m.r. of the solution exhibited a peak (844%) due to triethyl phosphate and another peak at +18.7 p.p.m. (562%). The solvent was removed under reduced pressure, leaving an oil (1.82 g) which was subjected to lplc.

Elution with petrol/ether (100:10) gave an unidentified yellow oil (0.019 g). Further elution gave a yellow oil (0.162 g) which was distilled by bulb distillation to give 2-(2,4,6-trimethylphenyl)-3-phenyl-2H-azirine (0.121 g; 14%) as a yellow oil, b.p. ca 120°C/0.1 mm; $\nu_{max}$ 1738 (C=N), 1614, 1487, 1451, 1326 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 2.22 (3H, s, p-$CH_3$), 2.36 (6H, s, o-$CH_3$), 3.29 (1H, s), 6.76 (2H, s, m-ArH), 7.42-7.60 (3H, m, PhH), 7.82-8.00 (2H, m, o-PhH); $\delta_C$ ($CDCl_3$): 169.9 (C=N), 137.8, 136.5, 136.3, 133.0, 132.6, 129.4, 129.1, 126.7, 32.8 (N-CH), 21.1 (o-$CH_3$), 20.8 p.p.m. (p-$CH_3$). (Found: C, 87.0; H, 7.3; N, 5.9%. $C_{17}H_{17}N$ requires C, 86.8; H, 7.3; N, 5.9%). m/e 235 ($M^+$, 100%), 220 (6), 132 (81), 117 (68); $m^*$ 103.7 (132 -> 117).

Elution with petrol/ether (100:25) gave an unidentified yellow-brown oil (0.033 g). Further elution gave an off-white solid (0.113 g) identified as N-phenyl-2-(2,4,6-trimethylphenyl)acetamide (12%), m.p. 199.5-200°C from ethanol (66% recovery); $\nu_{max}$ 3270 (NH), 1659 $cm^{-1}$ (CO); $\delta_H$ ($CDCl_3$): 2.28 (9H, s, $CH_3$), 3.71 (2H, s, $CH_2$), 6.90 (2H, s, m-ArH), 6.98-7.42 (6H, m, PhH + NH). (Found: C, 80.3; H, 7.4; N, 5.3%. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.6; N, 5.5%). m/e 253 ($M^+$, 53%), 160 (50), 134 (43), 133 ($ArCH_2$, 100), 119 (PhNCO, 22), 93 ($PhNH_2$, 69); $m^*$ 105.7 (134 -> 119), 101.2 (253 -> 160).

(3) 5,5,5-Triethoxy-4,5-dihydro-4-(4-methylphenyl)-3-phenyl-1,2,5-oxazaphosph(v)ole.

A solution of 80% pure phosph(v)ole (1.50 g; 3.85 mmol if pure) in t-butylbenzene (20 ml) was added dropwise over a period of 15 min to refluxing t-butylbenzene (10 ml) under nitrogen. After the addition was complete, the solution was heated under reflux for a further 5 min, giving

a bright yellow solution. $^{31}P$ N. m. r. showed no phosph(v)ole remaining, but showed five peaks in the P=O region, one of them due to triethyl phosphate. The yield of phosphate was ca 10%. The solvent was removed from the solution under reduced pressure, leaving an oil (1.60 g) which was chromatographed on silica under low pressure.

Elution with ether gave a yellow oil (0.213 g) which yielded an oily brown solid (0.015 g) after removal of residual t-butylbenzene in vacuo. Tlc indicated that the solid was a mixture of several components, including 6-methyl-2-phenylindole, but the amount of indole was shown to be small (<1%) by $^{1}H$ n. m. r.

Further elution with ether gave a yellow oil (0.777 g) which was distilled by bulb distillation (92% recovery) to give another yellow oil (0.713 g), b.p. ca 160°C/0.01 mm. The oil was found to be a mixture, but consisting principally of one compon ent identified as diethyl 1-(4-methylphenyl)-N-phenylketenimine-1-phosphonate (ca 50%); I.R. exhibited the following features, which are attributed to the two components of the mixture. The first group of signals is very strong. $\nu_{max}$ (1) 2020 (C=C=N), 1255 (P=O), 1050 (POC), 1020 $cm^{-1}$ (POC), $\nu_{max}$ (2) 3500 (broad) (NH ?), 1666 $cm^{-1}$ (C=O ?); $\delta_H$ ($CDCl_3$): 1.29 (6H, t, $J_{HH}$ = 7 Hz, $CH_3$), 2.30 (3H, s, $CH_3$), 4.17 (4H, quintet, collapses to q on irradiation at the phosphorus frequency, $J_{HH}$ = 7 Hz, $J_{PH}$ = 7 Hz, $CH_2$), 7.20 (4H, AB quartet, ArH), 7.32 (5H, s, PhH); $\delta_P$ ($CDCl_3$): +20.0 (6213%), +20.5 p.p.m. (485%); the salient features of the $^{13}C$ n.m.r. are as follows. $\delta_C$ ($CDCl_3$): 177.9 (d, $J_{PC}$ = 10.0 Hz, P-C=C=N), 137.4 (d, $J_{PC}$ = 5.8 Hz, C-C-P), 135.7 (s, C-N), 62.3 (d, $J_{PC}$ = 5.6 Hz, $CH_2$), 60.2 (d, $J_{PC}$ = 197 Hz, P-C=C), 20.7 (s, $CH_3$), 16.0 p.p.m. (d, $J_{PC}$ =

6.8 Hz, $CH_3$). m/e 389 (10%), 343 ($M^+$, 100), 315 (8), 287 (12), 269 (17), 242 (16), 207 (17), 196 (28), 168 (26), 103 (42); $m^*$ 289.3 (343 -> 315), 261.5 (315 -> 287), 252.1 (287 -> 269), 144.0 (196 -> 168), 112.0 (343 -> 196). (Found: $M^+$, 343.132935. $C_{19}H_{22}NO_3P$ requires M, 343.133723). A second distillation (140°C/0.01 mm) did not increase the purity of the product.

Further elution with ether gave a brown oil (0.29 g) which was shown by $^{31}P$ n.m.r. to be a mixture of four components.

The ketenimine was dissolved in ethanol and left at room temperature for a few days, with and without an added crystal of p-toluenesulphonic acid. In neither case was there found to be any significant reaction.

The ketenimine (0.146 g; 0.426 mmol) was dissolved in acetone (4 ml) and 4M hydrochloric acid (1 ml) added. The solution was allowed to stand at room temperature for 28 h, and then added to a large volume of water giving a white precipitate of diethyl N-phenyl-2-(4-methylphenyl)-acetamide-2-phosphonate (0.124 g; 81%), m.p. 121-122°C; $\nu_{max}$ 3260 (NH), 3200 (NH), 3140, 1688 (CO), 1602, 1555 (CO), 1240 (PO), 1053 (POC), 1021 $cm^{-1}$ (POC); $\delta_H$ ($CDCl_3$): 1.15 (3H, t, $J_{HH}$ = 7 Hz, $CH_3$), 1.25 (3H, t, $J_{HH}$ = 7 Hz, $CH_3$), 2.30 (3H, s, $CH_3$), 3.74-4.30 (4H, m, simplified on irradiation at the phosphorus frequency, $CH_2$), 4.26 (1H, d, $J_{PH}$ = 24 Hz, CH-P), 6.90-7.64 (9H, m, ArH), 9.28 (1H, broad s, NH); $\delta_P$ ($CDCl_3$): +22.1 p.p.m. (Found: C, 63.2; H, 6.8; N, 4.0%. $C_{19}H_{24}NO_4P$ requires C, 63.1; H, 6.7; N, 3.9%). m/e 361 ($M^+$, 21%), 242 (M-PhNCO, 100), 214 (14), 186 (18), 132 (10), 121 (7), 119 (PhNCO, 8), 105 ($CH_3C_6H_5CH$, 40), 93 ($PhNH_2$, 11); $m^*$ 162.2 (361 -> 242),

189.2 (242 -> 214).

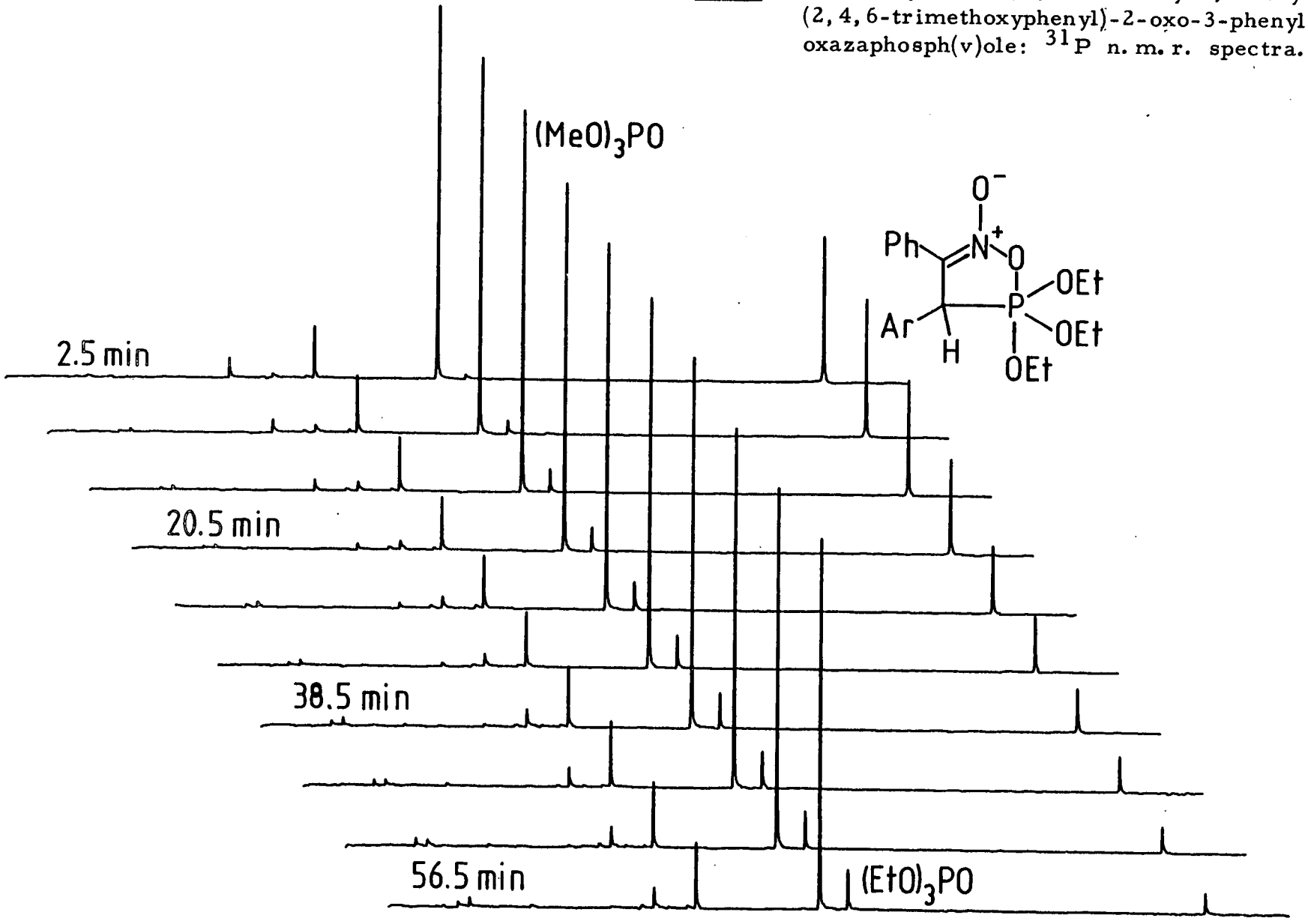
(4) 5,5,5-Triethoxy-4,5-dihydro-4-(2,4,6-trimethoxyphenyl)-2-oxo-3-phenyl-1,2,5-oxazaphosph(v)ole

A mixture of the phosph(v)ole (0.096 g; 0.2 mmol) and t-butylbenzene (0.3 ml) was heated in an n.m.r. tube under nitrogen at 154°C for 30s. On cooling, a yellow precipitate slowly formed. $^{31}$P N.m.r. of the solution showed two main peaks at -0.8 p.p.m. and -26.0 p.p.m. due to triethyl phosphate and 5,5,5-triethoxy-4,5-dihydro-4-(2,4,6-trimethoxyphenyl)-3-phenyl-1,2,5-oxazaphosph(v)ole respectively. This was confirmed by "spiking" the solution with an authentic sample of each product. There was also a small peak at -23.5 p.p.m. The yellow precipitate was identified as 2-(2,4,6-trimethoxyphenyl)-1-phenylnitroethene (0.023 g; 73%) by tlc and $^{1}$H n.m.r. The solid melted over a wide range, and its U.V. spectrum and h.p.l.c. (2:1 hexane/ethyl acetate + 1% ethanol) suggested it was a mixture of the E- and Z-isomers.

(5) Kinetics of the thermolysis of 5,5,5-triethoxy-4,5-dihydro-4-(2,4,6-trimethoxyphenyl)-2-oxo-3-phenyl-1,2,5-oxazaphosph(v)ole.

The phosph(v)ole (0.0472 g; 0.098 mmol) was dissolved in $d_6$-benzene (0.3 ml) and trimethyl phosphate (0.0200 g; 0.143 mmol) added as the standard. The solution was put in an n.m.r. tube filled with nitrogen, and the reaction followed in the FX-60 probe at 76°C. The spectral parameters were as follows.

Fig. 1 Thermolysis of 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole: $^{31}P$ n. m. r. spectra.



Spectral width 2500 Hz

Window parameter 12

Number of transients 100

Pulse repeat 1.8s

Wait time 180s

Initial $^{31}P$ n.m.r. at room temperature showed the presence of the phosph(v)ole, trimethyl phosphate, and a small impurity peak at +16.3 p.p.m. due to an impurity in the phosphate. Recording of spectra was started at t = 1 min. The time interval between the start of successive recordings was 6 min. The resultant spectra are shown in Fig. 1. The results are also tabulated in Table 3. A plot of ln (y/x) against t is a straight line (Fig. 2), indicating

TABLE 3

Kinetics of Phosph(v)ole Thermolysis

| | Peak areas (%) | | | |
|---|---|---|---|---|
| t/min | Phosphate (x) | Phosph(v)ole (y) | ln (y/x) | x/y |
| 2.5 | 8274 | 3030 | -1.005 | 2.731 |
| 8.5 | 8035 | 3069 | -0.962 | 2.618 |
| 14.5 | 8230 | 2529 | -1.180 | 3.254 |
| 20.5 | 7944 | 2031 | -1.364 | 3.911 |
| 26.5 | 7875 | 1517 | -1.647 | 5.191 |
| 32.5 | 7916 | 1185 | -1.899 | 6.680 |
| 38.5 | 7896 | 1005 | -2.061 | 7.857 |
| 44.5 | 7598 | 837 | -2.206 | 9.078 |
| 50.5 | 7566 | 631 | -2.484 | 11.990 |
| 56.5 | 7696 | 498 | -2.738 | 15.454 |

first order kinetics. The second order plot (x/y against t) is a curve.

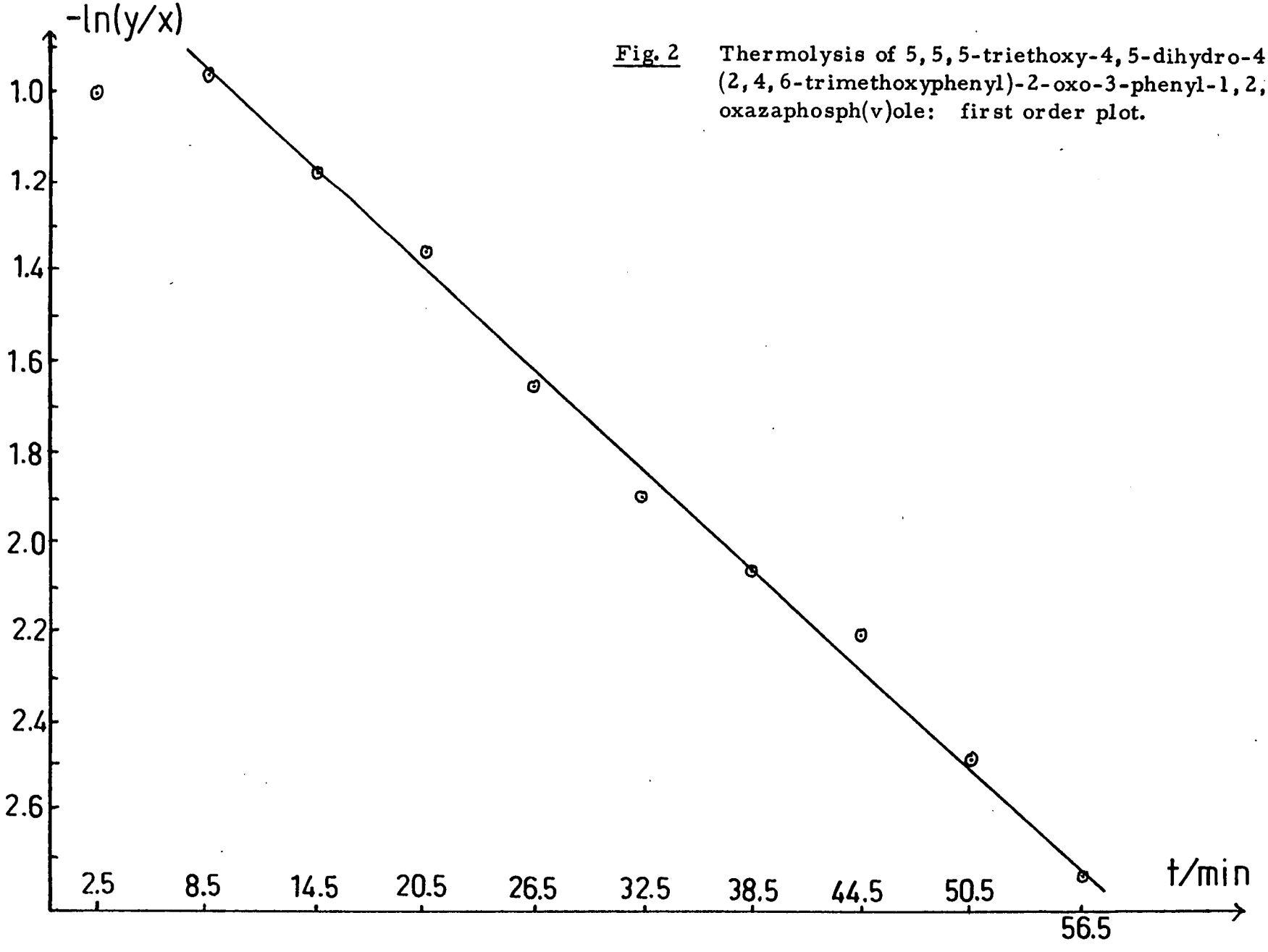



Fig. 2 Thermolysis of 5,5,5-triethoxy-4,5-dihydro-4-(2,4,6-trimethoxyphenyl)-2-oxo-3-phenyl-1,2,5-oxazaphosph(v)ole: first order plot.

Ignoring the first point, a least squares program gives the first order rate constant as

$$k_{349} = (6.07 \pm 0.14) \times 10^{-4}\ s^{-1}.$$

K. Reactions Concerning 2-Aryl-1-phenylnitrosoethenes.

(1) Attempted Preparation of 1, 2-Diphenyl-1-nitrosoethene

(a) Dehydrochlorination of 1-chloro-1, 2-diphenyl-2-nitrosoethane dimer.

(i) The nitrosoethane dimer (2.20 g; 9 mmol), pyridine (5 ml; excess) and methanol (200 ml) were heated under reflux under nitrogen for 3.5 h. Unreacted nitrosoethane (0.79 g; 36%), identified by its I.R. spectrum, was filtered off and the yellow filtrate evaporated under reduced pressure. The solid residue was shaken with water and then extracted with chloroform. The extracts were washed with dilute hydrochloric acid, water, aqueous potassium bicarbonate, and finally water to neutrality. After drying, the solution was evaporated under reduced pressure giving a brown tarry residue from which no identifiable products could be obtained.

(ii) A mixture of the nitrosoethane dimer (2.20 g; 9.0 mmol) and 1, 5-diazabicyclo[5.4.0]undec-5-ene (DBU) (1.40 g; 9.2 mmol) in dimethyl sulphoxide (100 ml) was heated at 70-80°C for 16 h. As much as possible of the solvent was removed under reduced pressure, leaving a yellow-brown oil. Tlc of the oil showed a minimum of six products. Trituration and recrystallisation were both unsuccessful. Bulb distillation (81°C/0.9 mm) of the oil gave only residual DMSO. The residue was chromatographed on alumina but only unidentified oils were obtained.

(iii) A suspension of the nitrosoethane dimer (0.88 g; 3.6 mmol) and anhydrous sodium carbonate (0.38 g; 3.6 mmol) in dichloromethane (130 ml) was heated under reflux for 8 h. A residual solid (0.35 g) was filtered off, and this was shown by I.R. to contain sodium carbonate. The solution was evaporated under reduced pressure giving a yellow solid which was recrystallised from chloroform to give a white solid (0.06 g), m.p. 226-229°C, decomp.; $\nu_{max}$ 1550 ($NO_2$), 1365 $cm^{-1}$ ($NO_2$). The mass spectrum exhibits m/e 225 with the base peak at 179.

(iv) To a solution of [18]crown-6 polyether (1.05 g; 4 mmol) in dichloromethane (100 ml) was added anhydrous potassium carbonate (0.55 g; 4 mmol) and a little methanol (1 ml) to assist solubilisation.[212] The nitrosoethane dimer (1.97 g; 8 mmol) was then added and the mixture heated under reflux under nitrogen for 66 h, giving an orange solution. A white solid (0.36 g) which was filtered off was found by I.R. to contain potassium carbonate. Removal of the solvent under reduced pressure gave a brown oil which was washed with water to remove water-soluble material, extracted with dichloromethane, and dried. Evaporation of the solvent again gave an oil, which was triturated with ether to give a brick-red solid (0.16 g), m.p. 116-121°C. $^1$H N.m.r. suggested that the solid was mainly [18]crown-6 ; however, there was also a positive flame test for potassium and a positive chloride ion test. The remaining oil (1.95 g) was chromatographed on alumina using the dry column technique with chloroform as the eluant. Stilbene (0.28 g), identified by its I.R. spectrum, was obtained in addition to several intractable oils.

(v) A solution of N, N-dimethylaniline (0.61 g; 5 mmol) in ether (125 ml) was heated under reflux under nitrogen and reacted with the nitrosoethane dimer (1.23 g; 5 mmol) contained in a soxhlet thimble. No significant

reaction was observed after 10 h, however.

The experiment was repeated with methanol as the solvent. After 23 h reflux, a dirty green solution was obtained, although much of the dimer remained unchanged. On evaporation of the solvent, a very dark green oil was obtained and this yielded only an unidentified sticky yellow solid on vacuum sublimation.

(b) Attempted preparation of α-chloro-α-phenylacetophenone oxime

(i) α-Benzoin oxime (2.95 g; 13 mmol) was suspended in chloroform (100 ml) and a solution of thionyl chloride (2.14 g; 18 mmol) in chloroform (30 ml) added slowly with stirring. The mixture was stirred overnight at room temperature giving a colourless solution. Removal of the solvent under reduced pressure gave an almost colourless liquid (2.37 g) which was shown by I.R. to be a mixture of benzaldehyde and benzonitrile.

(ii) A solution of hydroxylamine hydrochloride (1.39 g; 20 mmol) in water (5 ml) was neutralised with a solution of sodium hydroxide (0.80 g; 20 mmol) in water (5 ml) and added to a solution of desyl chloride (2.31 g; 10 mmol) in ethanol (25 ml). The mixture was heated under reflux for 1.5 h, and the resultant clear solution added to water giving a very sticky off-white solid. The water was decanted off and the solid extracted with chloroform leaving an insoluble off-white solid, (0.16 g) which was shown to be a mixture by tlc. The I.R. spectrum suggested the possible presence of the oxime. The chloroform extracts were dried and the solvent removed under reduced pressure giving a yellow oil, which was shown by tlc to be a mixture of at least eight components.

(c) Attempted dehydration of α-benzoin oxime

α-Benzoin oxime (0.41 g; 1.8 mmol) was suspended in dichloromethane (25 ml) and acetic anhydride (0.21 ml; excess) added. The mixture was stirred for 2 h under nitrogen, giving an almost colourless solution. Removal of the solvent under reduced pressure gave an off-white solid (0.51 g), m.p. 108-110°C; $\nu_{max}$ 3400 (OH), 1762 $cm^{-1}$ (CO); $\delta_H$ ($CDCl_3$): 1.99 (3H, s, $CH_3$), 4.37 (1H, broad s, OH), 5.73 (1H, s, CH), 6.70-7.50 (10H, m, PhH). m/e 311 (0.2%), 269 (0.6), 209 (14), 179 (49), 162 (13), 103 (100).

Attempted thermal decomposition of this product using a Kugelrohr bulb distillation apparatus gave no identifiable products.

(d) Attempted oximation of benzoin tosylate

To a suspension of benzoin tosylate (1.95 g; 5.3 mmol) in ethanol (50 ml) was added a solution of hydroxylamine hydrochloride (0.97 g; 14 mmol) in water (10 ml). The mixture was stirred overnight at room temperature and a white solid filtered off and dried. The solid was shown by I.R. to be unreacted benzoin tosylate (1.27 g; 65%). Addition of water to the filtrate yielded more benzoin tosylate (0.32 g; 16%).

(e) Electrolytic reduction of 1, 2-diphenyl-1-nitroethene

A preliminary polarographic study of the reduction was carried out using 1N sulphuric acid/ethanol (1:1) as the backing electrolyte, and a cell concentration of the nitroethene of 2mM. The polarogram showed the half-wave potential to be ca -0.15V. Addition of an equimolar amount of benzene sulphinic acid had no effect on the polarogram, indicating that the sulphinic acid was not electroactive.

A preparative scale reduction was then attempted in the presence of benzene sulphinic acid. The cell used was a two compartment cell with a sintered glass disc, a platinum anode, and a stirred mercury pool cathode. Controlled potential electrolysis at -0.5V (relative to the standard calomel electrode) was employed. The reduction was carried out at 0°C in 1N sulphuric acid/ethanol (1:1) containing the nitroethene (0.23 g; 1.0 mmol) and the sodium salt of benzene sulphinic acid (0.20 g; 1.0 mmol). The reduction was followed using a coulometer. After ca 5 h, the current had fallen to the background level (2mA) and the volume change indicated by the coulometer represented a reduction involving 4F $mol^{-1}$.

The solution was then worked up by neutralising with potassium carbonate and extracting several times with ether. The combined extracts were then dried over anhydrous potassium carbonate and the solvent removed under reduced pressure giving an oily brown solid (0.08 g); $\nu_{max}$ 3330 (broad) (OH), 1684 $cm^{-1}$ (CO). m/e 211, 196, 193, 105 (base peak); $m^*$ 176.5 (211 -> 193), 56.3 (196 -> 105).

(f) Oxidation of phenylbenzyl ketimine

Phenylbenzyl ketimine (0.98 g; 5 mmol) was dissolved in benzene (50 ml) and the silver carbonate on celite reagent (6 g) added. The mixture was stirred for 30 min under nitrogen giving a dirty purple solution. Removal of the solvent under reduced pressure gave a deep brownish-purple solid which was recrystallised from ethanol to give deoxybenzoin (0.21 g), identified by its I.R. spectrum. m/e 196, 105; $m^*$ 56.3 (196 -> 105). Evaporation of the solvent from the mother liquors gave an oily solid which exhibited the following features. The I.R. spectrum showed a broad absorption at 3360 $cm^{-1}$, a small absorption at 2235 $cm^{-1}$, and also an

absorption at 1680 $cm^{-1}$. The mass spectrum exhibited m/e 196, 121, 105; $m^{*}$ 56.3 (196 -> 105).

(2) Nitroso Intermediacy in the Thermolysis of 2-Oxo-1, 2, 5-oxazaphosph(v)oles.

(a) Thermolysis of 4, 5-dihydro-5, 5, 5-trimethoxy-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole in 2, 5-dimethylfuran.

The phosph(v)ole (0.76 g; 2 mmol) was heated under reflux with 2, 5-dimethylfuran (5 ml; excess) under nitrogen for 17 h. Excess 2, 5-dimethylfuran was removed under reduced pressure giving a black tar (1.02 g) which was shown by tlc to contain a large number of products. Lplc failed to give any identifiable products.

(b) Thermolysis of 5, 5, 5-triethoxy-4, 5-dihydro-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole in the presence of thebaine.

A solution of the phosph(v)ole (1.22 g; 3 mmol) in benzene (20 ml) was added dropwise over a period of 1 h under nitrogen to a refluxing solution of thebaine (0.93 g; 3 mmol) in benzene (25 ml). The solution was heated under reflux for a further 20 min, after which $^{31}P$ n.m.r. showed the presence of triethyl phosphate and four other components. The benzene was removed under reduced pressure and the residue triturated with ether, giving a fawn solid (1.01 g). Further solid (0.13 g) precipitated from the ether solution on standing. Tlc showed these to be complex mixtures of products, and $^{1}H$ n.m.r. suggested their principal constituent was thebaine. Convincing evidence for the presence of an adduct was lacking. $^{31}P$ N.m.r. showed the presence of three phosphorus-containing compounds. The mass

spectrum exhibited only a very tiny 'blip' at the position expected for the adduct.

(c) Deoxygenation of 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole with dimethyl phenylphosphonite.

A mixture of the phosph(v)ole (0.096 g; 0.2 mmol) and dimethyl phenylphosphonite (0.3 ml) was heated under nitrogen in an n.m.r. tube.

(i) After 210s at 100°C, $^{31}$P n.m.r. of the solution showed,amongst others, peaks due to triethyl phosphite (209%), dimethyl phenylphosphonate (305%), triethyl phosphate (209%), the original phosph(v)ole (1002%) and a product at -16.5 p.p.m. (414%). Spiking the solution with 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-3-phenyl-1, 2, 5-oxazaphosph(v)ole produced a peak at -26.0 p.p.m.

In a control experiment, reaction between dimethyl phenylphosphonite and 5, 5, 5-triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-3-phenyl-1, 2, 5-oxazaphosph(v)ole after 210s at 100°C gave no peak at -16.5 p.p.m. in the $^{31}$P n.m.r. spectrum.

(ii) After 30s at 154°C, $^{31}$P n.m.r. showed essentially the same features as above, except that there was now a small peak at -26.0 p.p.m., and the peaks at -16.5 p.p.m. and due to the original phosph(v)ole were also small.

A control experiment showed that there was no reaction between triethyl phosphate and dimethyl phenylphosphonite after 30s at 154°C.

## L. Variable Temperature $^1$H N.M.R. Studies on 1, 2, 5-Oxazaphosph(v)oles

General method. The phosph(v)ole (ca 40 mg) was dissolved in the appropriate solvent (ca 0.4 ml) in a 5 mm n.m.r. tube and the temperature of the sample adjusted in the spectrometer probe. The temperature was allowed to stabilise before spectra were recorded. The coalescence temperature ($T_c$) was judged to be the temperature at which separate peaks merged to become just indistinguishable. The exact temperature was found by calibration against the chemical shift difference between the methyl and hydroxyl protons of a methanol standard.

The free energy of activation ($\Delta G^*$) for two-site exchange processes was calculated by a combination of a simplified Gutowsky-Holm equation[213] for the situation at the coalescence temperature ($2\pi\tau\Delta\nu = \sqrt{2}$, where $\tau$ is half the lifetime of either site and $\Delta\nu$ is the frequency difference between the separated resonances at slow exchange) and the Eyring equation[214] ($k' = (\sigma kT/h) \exp(-\Delta G^*/RT)$, where $\sigma$ is the transmission coefficient, $k'$ is the rate constant for the exchange process, and other symbols are conventional). Thus $k' = \pi\Delta\nu/\sqrt{2}$ and hence $\Delta G^* = RT \ln\left(\frac{\sigma kT\sqrt{2}}{\pi \Delta\nu\, h}\right)$ The transmission coefficient is generally taken as unity, and this will be the case in the examples quoted here. The above relation for $\Delta G^*$ strictly only applies to the coalescence of equally populated peaks but it will suffice for the present purpose. The value of $\Delta G^*$ for three-site exchange processes was not calculated as this would involve a complete line-shape analysis.

(1) 4, 5-Dihydro-5, 5, 5-trimethoxy-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

The solvent was dichloromethane. At 28°C, the methyl region of the

spectrum exhibits a singlet (3.74δ) due to the aromatic methoxyl group and a doublet (3.64δ; $J_{PH}$ = 12.5 Hz) due to the methoxyls attached to phosphorus. At -30°C, the doublet was replaced by a broad mound. At -40°C (judged to be $T_c$), a very broad, low mound resulted. At -50°C, a new peak structure was evident, and this became clear at -60°C as three separate broad doublets. At -70°C, the relevant parameters were δ: 3.84 (d, $J_{PH}$ = 14.5 Hz), 3.71 (d, $J_{PH}$ = 11.5 Hz), 3.34 (d, $J_{PH}$ = 11.0 Hz). The aryl methoxyl signal remains a singlet, but shifts upfield by 3.4 Hz on changing the temperature from +28°C to -70°C.

(2) 4, 5-Dihydro-5, 5, 5-trimethoxy-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole

The solvent was dichloromethane. At 28°C, the spectrum shows a doublet at 3.69δ ($J_{PH}$ = 12.2 Hz) due to the methoxyl groups and a doublet at 2.33δ ($J_{PH}$ = 2.8 Hz) due to the aryl methyl group. At -80°C, a new peak structure has appeared as three broad doublets, δ : 3.81 (d, $J_{PH}$ = 13 Hz), 3.68 (d, $J_{PH}$ = 12.2 Hz), 3.28 (d, $J_{PH}$ = 10.7 Hz). The doublet due to the aryl methyl group is significantly broadened. The doublets all collapse to singlets on irradiation at the phosphorus frequency. The coalescence temperature was judged to be -37°C.

(3) 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5, 5-trimethoxy-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

The solvent was dichloromethane. At 28°C, the methoxyl groups appear as a sharp doublet at 3.63δ ($J_{PH}$ = 12.8 Hz). At -85°C, a new peak structure has formed, consisting of three doublets, δ : 3.79 (d, ($J_{PH}$ = 15.0 Hz), 3.66 (d, $J_{PH}$ = 12.7 Hz), 3.28 (d, $J_{PH}$ = 11.0 Hz).

These doublets collapse to singlets on irradiation at the phosphorus frequency. At -46°C, the room temperature doublet has been replaced by two broad humps. At -60°C, the new peak structure is becoming evident. $T_c$ was judged to be -50°C.

(4) 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5-dimethoxy-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole.

The solvent was deuteriochloroform. At -40°C, peaks due to two isomers are observed. The major isomer exhibited peaks at $\delta$ : 4.85 (d, $J_{PH}$ = 17.5 Hz), 3.91 (d, $J_{PH}$ = 12.5 Hz), 3.14 (d, $J_{PH}$ = 10.5 Hz), and the minor isomer exhibited peaks at $\delta$ : 5.00 (d, $J_{PH}$ = 25.5 Hz), 4.18 (d, $J_{PH}$ = 13.5 Hz), and 3.05 (d, $J_{PH}$ = 10.2 Hz). There were also multiplets at 7.10-7.68$\delta$ and 7.81-8.20$\delta$. Each set of doublets collapses to singlets on irradiation at its particular phosphorus irradiation frequency. As the temperature is raised, the lines broaden and come together. For the methoxyl groups, $T_c$ was judged to be 40$\pm$ 2°C and $\Delta\nu$ was 8.9 Hz. This gives $\Delta G^* = 69 \pm 0.5$ kJ mol$^{-1}$. Coalescence of the signals due to the $sp^3$ proton adjacent to the phosphorus was judged to occur at 15$\pm$3°C. $\Delta\nu$ was 15.6 Hz and so $\Delta G^* = 62 \pm 1$ kJ mol$^{-1}$. At 60°C, the lines had sharpened and the spectrum exhibited the following features. $\delta$ : 3.72 (d, $J_{PH}$ = 11 Hz, $OCH_3$), 4.83 (d, $J_{PH}$ = 22 Hz, CH-P).

(5) 4, 5-Dihydro-5, 5-dimethoxy-4-(4-methoxyphenyl)-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole.

The solvent was deuteriochloroform. At -40°C, doublets due to two isomers are observed. Each set of doublets collapses to singlets at its irradiation frequency. These signals broaden and come together as the

temperature is raised. For the methoxyl groups, $T_c$ was $56 \pm 2^{\circ}C$, and $\Delta\nu = 9.4$ Hz. This gives $\Delta G^{*} = 73 \pm 0.5$ kJ mol$^{-1}$. For the $sp^3$ hydrogen atom, $T_c = 25 \pm 4^{\circ}C$, $\Delta\nu = 14$ Hz, and so $\Delta G^{*} = 64 \pm 1$ kJ mol$^{-1}$.

(6) 4, 5-Dihydro-5, 5-dimethoxy-4-(4-methylphenyl)-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole

The solvent was deuteriochloroform. At $-30^{\circ}C$, doublets due to two isomers are observed, and these collapse to singlets on irradiation at their particular phosphorus frequency. The signals broaden and come together as the temperature is raised. For the methoxyl protons, $T_c = 50 \pm 1^{\circ}C$ and $\Delta\nu = 7.8$ Hz, giving $\Delta G^{*} = 72 \pm 0.5$ kJ mol$^{-1}$. For the $sp^3$ proton, $T_c = 13 \pm 5^{\circ}C$, $\Delta\nu = 14$ Hz, and hence $\Delta G^{*} = 62 \pm 1$ kJ mol$^{-1}$.

(7) 5, 5, 5-Triethoxy-4, 5-dihydro-4-(2, 4, 6-trimethoxyphenyl)-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

The solvent was deuteriochloroform. At $28^{\circ}C$ (see section I(1)), the signals due to the m-aryl protons and the o-methoxyl protons are broad and non-equivalent. At $-40^{\circ}C$, the signals are sharper and $\Delta\nu = 21.5$ Hz for the m-protons, and for the o-methoxyl protons, $\Delta\nu = 31.5$ Hz. For the aryl protons, $T_c$ was judged to be $47 \pm 1^{\circ}C$, giving $\Delta G^{*} = 68 \pm 0.5$ kJ mol$^{-1}$. The changes in the methoxyl region of the spectrum were difficult to observe due to overlap with the methylene signals. $T_c$ for the methoxyl protons was estimated as $47 \pm 10^{\circ}C$, and hence $\Delta G^{*} = 67 \pm 2$ kJ mol$^{-1}$. At $63^{\circ}C$, the signals begin to peak.

M. Reactions with Fully Substituted Nitroethenes

(1) Deoxygenation of Z-2-ethyl-1, 2-diphenyl-1-nitroethene.

A mixture of the nitroethene (1.27 g; 5 mmol) and triethyl phosphite (3.5 ml; 20 mmol) was heated under reflux under nitrogen for 16 h. The solvent was then removed at 90°C/0.2 mm leaving a yellow oil (1.56 g) which was chromatographed on silica under low pressure.

Elution with petrol/ether (100:5) gave a yellow oil (0.054 g) identified as 1-ethoxyimino-1, 2-diphenylbut-2-ene (4.1%), b.p. ca 145°C/0.3 mm; $\nu_{max}$ 1600, 1496, 1447, 1381, 1360, 1287, 1090, 1058, 1040 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 1.25 (3H, t, $J_{HH}$ = 7 Hz, collapses to s on irradiation at 4.24δ, $CH_3$), 1.70 (3H, d, $J_{HH}$ = 7 Hz, collapses to s on irradiation at 6.37δ, $CH_3$), 4.24 (2H, q, $J_{HH}$ = 7 Hz, $CH_2$), 6.37 (1H, q, $J_{HH}$ = 7 Hz, CH), 7.10-7.45 (8H, m, PhH), 7.58-7.78 (2H, m, o-PhH). (Found: C, 81.6; H, 7.4; N, 5.1%. $C_{18}H_{19}NO$ requires C, 81.5; H, 7.2; N, 5.3%). m/e 265 ($M^+$, 63%), 250 (42), 236 (13), 220 (M-$C_2H_5O$, 100), 117 ($PhCCHCH_3$, 63), 115 ($PhCCCH_2$, 53); $m^*$ 235.8 (265 -> 250), 182.6 (265 -> 220), 113.0 (117 -> 115).

Elution with petrol/ether (100:10) gave a light brown solid (0.606 g) which recrystallised with difficulty from ethanol (33% recovery) to give off-white crystals (48% yield), m.p. 131-133°C, decomp.; $\nu_{max}$ 2500-3300 (chelated OH), 1539 $cm^{-1}$; $\delta_H$ ($CDCl_3$ + 5 drops $d_6$-DMSO): 0.44 (3H, t, $J_{HH}$ = 7.5 Hz, $CH_3$), 2.06 (2H, m, collapses to AB quartet on irradiation at 0.44δ, AB part of an $ABX_3$ system, $J_{AB}$ = 13 Hz, $J_{AX}$ = 7.5 Hz, $CH_2$), 7.14-7.62 (7H, m, PhH), 8.20-8.42 (2H, m, o-PhH), 11.53 (1H, sharp s, OH). The $^{13}C$ n.m.r. spectrum ($d_6$-DMSO) appeared to show two sets of peaks. After standing overnight, only one set of peaks remained. The

salient features of both sets are as follows. $\delta_C$ (1): 176.7*, 153.5*, 138.1*, 132.3*-127.8, 122.8, 97.6*, 27.3, 7.0 p.p.m.; $\delta_C$ (2): 179.7*, 153.0*, 142.3*, 132.4*-126.0, 122.3, 120.3, 87.1*, 31.5, 7.2 p.p.m. The off-resonance spectrum shows all the asterisked peaks to be quaternaries. All other carbon atoms in the region 120-132 p.p.m. have one proton attached. The analysis of the initial product was as follows. (Found: C, 76.1; H, 6.0; N, 5.4%. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%). m/e 253 ($M^+$, 37%), 236 (52), 224 (55), 206 (36), 196 (21), 179 (23), 105 (100); $m^*$ 198.3 (253 -> 224), 155.5 (206 -> 179). The compound which formed on standing in DMSO had the following n.m.r. $\delta_H$ ($d_6$-DMSO): 0.30 (3H, t, $J_{HH}$ = 8 Hz, $CH_3$), 1.75-2.38 (2H, m, $CH_2$), 6.21 (1H, s, OH), 7.14-7.75 (7H, m, PhH), 8.22-8.46 (2H, m, o-PhH). The DMSO was pumped off at room temperature, leaving an oil which yielded a small amount of an off-white solid on trituration with ether. The I.R. spectrum of the solid exhibited absorptions at 2140 $cm^{-1}$ and 2265 $cm^{-1}$, but these were weak in the spectrum of the remaining oil. The $^1H$ n.m.r. of the oil in $CDCl_3$ was essentially the same as in DMSO, except that the hydroxyl signal now appeared as a very broad hump at ca 4.6δ. The oil and the solid exhibited essentially the same mass spectrum: m/e 253 (1%), 237 (84), 222 (100), 208 (51), 133 (15), 105 (29).

Further elution with petrol/ether (100:10) gave a white solid (0.064 g) which was recrystallised from hexane (20% recovery) to give purple-surfaced needles tentatively identified as 5-methyl-2,3-diphenyl-3-isoxazoline (5.4%), m.p. 107-109.5°C; $\nu_{max}$ 1497, 1359 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 1.02 (3H, d, $J_{HH}$ = 6.4 Hz, $CH_3$), 4.48 (1H, d, $J_{HH}$ = 9.1 Hz, CH), 4.89 (1H, d of q, $J_{HH}$ = 6.4 Hz, 9.1 Hz, $CH_3$-CH-CH), 7.10 (2H, d, $J_{HH}$ = 6.9 Hz, PhH),

7.20-7.30 (6H, m, PhH), 7.55-7.58 (2H, m, PhH). (Found: $M^+$, 237.115516. $C_{16}H_{15}NO$ requires M, 237.115358). m/e 237 ($M^+$, 32%), 193 (M-$CH_3CHO$, 100), 165 (9), 116 (10), 90 (19); $m^*$ 157.2 (237 -> 193), 141.1 (193 -> 165); found, M, 193.089430. $C_{14}H_{11}N$ requires M, 193.089145. A satisfactory analysis was not obtained.

(2) Deoxygenation of Z-2-methyl-1,2-diphenyl-1-nitroethene

A mixture of the nitroethene (0.96 g; 4 mmol) and triethyl phosphite (2.8 ml; 16 mmol) was heated under reflux under nitrogen for 17.5 h giving an orange solution. Removal of the solvent gave a brown oily residue (1.20 g) which was chromatographed on silica. Elution with petrol/ether (100:20) gave a fawn solid (0.521 g) which recrystallised with difficulty from ethanol (21% recovery) to give an off-white solid (54% yield), m.p. 118-120°C; $\nu_{max}$ 2500-3250 (chelated OH), 1542 $cm^{-1}$; $\delta_H$ ($CDCl_3$ + 6 drops $d_6$-DMSO): 1.60 (3H, s, $CH_3$), 7.10-7.65 (7H, m, ArH), 8.22-8.48 (2H, m, o-PhH), 11.57 (1H, broad s, OH). After several days, a new singlet had appeared at 1.57δ and a broad singlet at 5.90δ. (Found: C, 75.0; H, 5.6; N, 5.7%. $C_{15}H_{13}NO_2$ requires C, 75.3; H, 5.4; N, 5.9%). m/e 239 ($M^+$, 27%), 223 (72), 222 (39), 208 (27), 196 (15), 193 (10), 105 (100); $m^*$ 160.7 (239 -> 196).

(3) Phosph(v)ole formation from Z-2-methyl-1,2-diphenyl-1-nitroethene

A mixture of the nitroethene (0.048 g; 0.2 mmol), triethyl phosphite (50 μl; excess) and tert-butanol (0.4 ml) was shaken on a mechanical shaker and the solution examined periodically by $^{31}P$ n.m.r. After 18 h, in addition to triethyl phosphite (7150%), $^{31}P$ n.m.r. showed the presence of triethyl phosphate (1105%) and the phosph(v)ole at -38.9 p.p.m. (1044%).

After 90 h, $^{31}$P n. m. r. showed principally triethyl phosphite (6716%), triethyl phosphate (1427%) and the phosph(v)ole (2288%). After 184 h, a new peak had appeared at 6. 8 p. p. m. (1738%). Also present were triethyl phosphite (6904%), triethyl phosphate (4687%) and the phosph(v)ole (6534%). Tlc showed the presence of unreacted nitroethene.

(4) Phosph(v)ole formation from Z-2-ethyl-1, 2-diphenyl-1-nitroethene.

Triethyl phosphite (50 µl; excess) was added to a mixture of the nitroethene (0. 051 g; 0. 2 mmol) and tert-butanol (0. 4 ml) in an n. m. r. tube, and the mixture shaken under nitrogen for 17 h. $^{31}$P N. m. r. showed the presence of mainly triethyl phosphite, a little triethyl phosphate, and a smaller amount of the expected phosph(v)ole (-40. 3 p. p. m. ). After 120 h, $^{31}$P n. m. r. showed a little more phosphate and phosph(v)ole, but a significant amount of insoluble nitroethene remained unchanged.

(5) Thermolysis of Z-2-ethyl-1, 2-diphenyl-1-nitroethene

A mixture of the nitroethene (0. 025 g; 0. 1 mmol) and the solvent (ca 0. 3 ml) was heated under nitrogen for 16 h. The solvent was then pumped off at room temperature and the residue examined by $^{1}$H n. m. r. and/or tlc.

(a) In t-butylbenzene at 156°C, a light brown solution was formed. The resultant light brown crystalline residue was shown by n. m. r. and tlc to be principally unreacted nitro ethene. There was only a very faint tlc spot corresponding to the unknown in section M(1).

(b) In t-butylbenzene with two drops of added triethyl phosphite at 156°C, the final product was a brown oil. Tlc showed the presence of unreacted nitroethene together with several products; however there was only a very

faint spot due to the unknown in M(1). The n. m. r. spectrum was not helpful.

(c) In pyridine in a boiling toluene bath, the final product was a brown oil. Tlc showed the presence of unreacted nitroethene plus several products, but no spot corresponding to the unknown in M(1).

## N. Acid Catalysed Hydrolysis of 4, 5-Dihydro-2-oxo-1, 2, 5-oxazaphosph(v)oles

General procedure. The aqueous acid used in the hydrolysis experiments was prepared from p-toluenesulphonic acid monohydrate (3. 044 g) in water, made up to 50 ml. The solution thus contains 0. 32 mmol per ml of p-toluenesulphonic acid. This was reacted with the phosph(v)ole in dioxan, and the final solution worked up as follows. The solvent was removed under reduced pressure and the residue redissolved in chloroform (50 ml), shaken with 1% aqueous sodium bicarbonate (2 x 40 ml), washed with water (3 x 40 ml), and dried. Removal of the solvent under reduced pressure then gave the product mixture.

### (1) 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5, 5-trimethoxy-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole

The phosph(v)ole (1. 92 g; 5 mmol) was dissolved in dioxan (39 ml) and aqueous p-toluenesulphonic acid (1 ml) added. The solution immediately went turquoise. $^{31}P$ N. m. r. showed no phosph(v)ole remaining after 30 min stirring. Work-up gave a yellow oil (1. 29 g) which was shown by $^{31}P$ n. m. r. to contain one major product. Trituration with hexane gave a fawn solid (1. 09 g) which was recrystallised from ethanol (57% recovery) to give

a white solid identified as dimethyl 2-(4-chlorophenyl)-1-phenylethan-1-one-2-phosphonate (64%), m.p. 136.5-137.5°C; $\nu_{max}$ 1682 (C=O), 1236 (P=O), 1064, 1032, 1019 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 3.67 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 3.74 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 5.32 (1H, d, $J_{PH}$ = 24 Hz, CH-P), 7.20-7.60 (7H, m, ArH), 7.82-8.00 (2H, m, o-PhH), $\delta_P$ ($CDCl_3$): +21.7 p.p.m. (Found: C, 56.4; H, 4.7%. $C_{16}H_{16}ClPO_4$ requires C, 56.7; H, 4.8%). m/e 340 ($M^+$, 11%), 338 ($M^+$, 31), 214 (7), 212 (20), 105 (PhCO, 100), 77 (51); found, M, 212.037317, 214.035410. $C_{14}H_9Cl$ requires 212.039275, 214.036325.

An earlier hydrolysis of this phosph(v)ole with 2M hydrochloric acid gave products which showed incorporation of chlorine from the acid.

(2) 4, 5-Dihydro-5, 5, 5-trimethoxy-4-(4-methylphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole.

The phosph(v)ole (1.82 g; 5 mmol) was dissolved in dioxan (78 ml) and aqueous p-toluenesulphonic acid (2 ml) added. The solution immediately turned blue, then rapidly went turquoise. After stirring for 30 min, the resultant yellow solution was worked up giving a yellow oil (1.70 g) which was shown by $^{31}P$ n.m.r. to be a mixture of several products. Trituration with ether gave an off-white solid (0.61 g) which was recrystallised from ethanol (73% recovery) to give white crystals identified as dimethyl 2-(4-methylphenyl)-1-phenylethan-1-one-2-phosphonate (38%), m.p. 151-152°C; $\nu_{max}$ 1679 (C=O), 1239 (P=O), 1059, 1025, 990 $cm^{-1}$; $\delta_H$ ($CDCl_3$): 2.29 (3H, d, $J_{PH}$ = 2Hz, $CH_3$), 3.67 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 3.74 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 5.30 (1H, d, $J_{PH}$ = 21 Hz, CH-P), 7.04-7.60 (7H, m, ArH), 7.84-8.03 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): +22.7 p.p.m. (Found: C, 64.3; H, 6.0%. $C_{17}H_{19}PO_4$ requires C, 64.1; H, 6.0%).

m/e 318 ($M^+$, 40%), 192 (13), 105 (100); $m^*$ 115.9 (318 -> 192), 34.7 (318 -> 105).

The trituration filtrate was evaporated giving a yellow oil which was chromatographed on silica under low pressure. Elution with ether/ethyl acetate (75:25) gave an off-white solid (0.174 g) which was recrystallised from ethanol (57% recovery) to give off-white crystals tentatively identified as dimethyl 7-methyl-3-phenyl-4H-1,2-benzoxazine-4-phosphonate (11%), m.p. 132-133°C; $\nu_{max}$ 1256 (P=O), 1053 (POC), 1017 $cm^{-1}$ (POC); $\delta_H$ ($CDCl_3$): 2.33 (3H, d, $J_{PH}$ = 2 Hz, $CH_3$), 3.48 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 3.54 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 4.71 (1H, d, $J_{PH}$ = 25 Hz, CH-P), 6.94 (1H, similar to half an AB pattern, J = 4 Hz, ArH), 6.97 (1H, broad s, slightly sharpened on irradiation at 2.3δ, ArH), 7.15 (1H, similar to half a phosphorus coupled AB pattern, J = 8 Hz, $J_{PH}$ = 2.5 Hz, ArH), 7.31-7.53 (3H, m, PhH), 7.81-8.04 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): +19.0 p.p.m.; $\delta_C$ ($CDCl_3$): 153.7* (d, $J_{PC}$ = 6.2 Hz), 153.0* (d, $J_{PC}$ = 4.9 Hz), 139.3* (d, $J_{PC}$ = 3.9 Hz), 132.9*, 130.5-125.3, 114.7 (d, $J_{PC}$ = 3.0 Hz), 111.4* (d, $J_{PC}$ = 8.7 Hz), 53.7 (d, $J_{PC}$ = 6.5 Hz), 37.2 (d, $J_{PC}$ = 142 Hz), 21.2 p.p.m.; the off-resonance spectrum suggests the asterisked peaks are quaternaries. (Found: C, 61.8; H, 5.5; N, 4.2%. $C_{17}H_{18}NO_4P$ requires C, 61.6; H, 5.5; N, 4.2%). m/e 331 ($M^+$, 88%), 299 (7), 228 (10), 222 (100), 213 (23), 194 (13), 170 (7), 109 (13), 103 (72); $m^*$ 270.1 (331 -> 299), 169.5 (222 -> 194), 157.1 (331 -> 228).

Further elution with ether/ethyl acetate (75:25) gave a light brown solid (0.100 g) which was shown by I.R. and tlc to be dimethyl 2-(4-methylphenyl)-1-phenylethan-1-one-2-phosphonate (6%).

(3) 4,5-Dihydro-5,5,5-trimethoxy-2-oxo-3,4-diphenyl-1,2,5-oxazaphosph(v)ole

The phosph(v)ole (1.75 g; 5 mmol) was dissolved in dioxan (39 ml) and aqueous p-toluenesulphonic acid (1 ml) added. The solution immediately turned blue, then rapidly went turquoise, then gradually green. The solution was stirred for 30 min, after which $^{31}P$ n.m.r. showed no remaining phosph(v)ole. Work-up of the solution gave an orange oil (1.90 g) which showed only two peaks in the $^{31}P$ n.m.r. spectrum. The oil was chromatographed on silica under low pressure. Elution with ether/ethyl acetate (75:25) gave a brown solid (0.147 g) which was recrystallised from ethanol (52% recovery) to give fawn needles tentatively identified as dimethyl 3-phenyl-4H-1,2-benzoxazine-4-phosphonate (9%), m.p. 118-119°C; $\nu_{max}$ 1254 (P=O), 1058 (POC), 1025 $cm^{-1}$ (POC); $\delta_H$ ($CDCl_3$): 3.49 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 3.57 (3H, d, $J_{PH}$ = 11 Hz, $CH_3O$), 4.76 (1H, d, $J_{PH}$ = 24 Hz, CH-P), 7.04-7.58 (7H, m, ArH), 7.80-8.05 (2H, m, o-PhH); $\delta_P$ ($CDCl_3$): +18.7 p.p.m. (Found: C, 60.6; H, 5.0; N, 4.2%. $C_{16}H_{16}NO_4P$ requires C, 60.6; H, 5.1; N, 4.4%). m/e 317 ($M^+$, 100%), 285 (11), 208 (66), 199 (15), 180 (17), 109 (13), 105 (26), 103 (56); $m^*$ 256.2 (317 -> 285), 155.8 (208 -> 180).

Further elution gave a light brown solid (0.610 g) which was recrystallised from ethanol (71% recovery) to give off-white crystals identified as dimethyl 1,2-diphenylethan-1-one-2-phosphonate (40%), m.p. 137-139°C (lit [195] 134-136°C); $\nu_{max}$ 1680 (C=O), 1240 (P=O), 1061, 1029, 1004, 992 $cm^{-1}$; $^1H$ n.m.r. as expected.

(4) 4,5-Dihydro-5,5,5-trimethoxy-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1,2,5-oxazaphosph(v)ole

The phosph(v)ole (1.90 g; 5 mmol) was dissolved in dioxan (39 ml) and aqueous p-toluenesulphonic acid (1 ml) added. The solution immediately went turquoise, and a white precipitate began to form after a short period of time. The mixture was stirred for 2 h giving a white precipitate and a yellow solution. The precipitate was identified as dimethyl 3-phenyl-2-isoxazoline-5-spirocyclohexadien-4'-one-4-phosphonate (0.955 g; 57%) obtained as white plates, m.p. 175.5-179°C, decomp. from acetonitrile (89% recovery); $\nu_{max}$ 1675 (C=O), 1636, 1250 (P=O), 1046 (POC), 1022 $cm^{-1}$ (POC); $\delta_H$ ($CDCl_3$): 3.46 (3H, d, $J_{PH}$ = 11.1 Hz, $CH_3O$), 3.64 (3H, d, $J_{PH}$ = 11.3 Hz, $CH_3O$), 4.08 (1H, d, $J_{PH}$ = 21.9 Hz, CH-P), 6.25 (1H, d of d of d, J = 1.8 Hz, 1.8 Hz, 10.2 Hz), 6.41 (1H, d of d, J = 1.8 Hz, 10.4 Hz), 6.88 (1H, d of d of d, J = 0.5 Hz, 3.1 Hz, 10.0 Hz), 7.40 (1H, d of d, J = 3.1 Hz, 10.5 Hz), 7.42-7.48 (3H, m, PhH), 7.73-7.75 (2H, m, o-PhH); $\delta_P$ ($CH_3CN$) (+72°C): +17.9 p.p.m.; $\delta_C$ ($CDCl_3$): 184.3 (C=O), 155.0 (d, $J_{PC}$ = 6.1 Hz, C=N), 143.8 (d, $J_{PC}$ = 14.6 Hz), 142.4 (d, $J_{PC}$ = 3.7 Hz), 130.8-128.0, 82.8, 54.8 (d, $J_{PC}$ = 142 Hz, C-P), 53.3 (m, $OCH_3$). (Found: C, 57.5; H, 4.9; N, 4.2%. $C_{16}H_{16}NO_5P$ requires C, 57.7; H, 4.8; N, 4.2%). m/e 333 ($M^+$, 75%), 303 (40), 165 (41), 119 (PhCNO, 100), 109 ($(CH_3O)_2PO$, 72), 105 (93), 103 (PhCN, 34), 93 (PhO, 69); $m^*$ 275.7 (333 -> 303); found, M, 303.078427. $C_{16}H_{16}O_4P$ requires 303.078615. Found: M, 165.071295. $C_{13}H_9$ requires 165.070422, $C_9H_{12}NP$ requires 165.070734. Attempted formation of the semicarbazone resulted in recovery of the starting material.

Work-up of the yellow solution gave an oily yellow solid (0.51 g) which

was recrystallised from acetonitrile to give a white solid (0.083 g) identified by I.R. as the spirodienone (5%), m.p. 177-180°C, decomp.

(5) $^{31}$P N.m.r. study of the hydrolysis of 4, 5-dihydro-5, 5, 5-trimethoxy-2-oxo-3, 4-diphenyl-1, 2, 5-oxazaphosph(v)ole.

The phosph(v)ole (0.035 g; 0.1 mmol) was dissolved in dioxan (0.4 ml) and aqueous p-toluenesulphonic acid (20 µl) added. The reaction was followed in the $^{31}$P n.m.r. probe. A significant amount of reaction was observed after only 2 min. The amount of phosph(v)ole decreased steadily to be replaced by a principal peak at +22.5 p.p.m. in addition to several smaller peaks. No other peaks were observed in the phosphorane region of the spectrum. The phosph(v)ole had all reacted after 32 min.

(6) $^{1}$H N.m.r. study of phosph(v)ole hydrolysis

Aqueous p-toluenesulphonic acid was prepared by dissolving p-toluenesulphonic acid monohydrate (0.0609 g; 0.32 mmol) in deuterium oxide (1 ml). The phosph(v)ole (0.1 mmol) was dissolved in $d_8$-dioxan (0.3 ml) and the aqueous acid (20 µl) added. The reaction was followed in the $^{1}$H n.m.r. probe.

(a) 4, 5-Dihydro-5, 5, 5-trimethoxy-2-oxo-3, 4-diphenyl-1, 2, 5-oxaza-phosph(v)ole. After 4.25 min, the phosph(v)ole doublet was at 4.79δ and product doublets had appeared at 5.57 δ (main product) and 5.02 δ. A large peak also appeared at 3.26δ . These peaks increased in size relative to the phosph(v)ole doublet, as did a singlet at 4.00 δ. After 34.5 min, the majority of the phosph(v)ole had reacted. The integrals of the product doubletsat 5.57 δ and 5.02 δ, and the singlet at 3.26 δ were respectively in the ratio 7.5:3:39. Spiking the solution with methanol (2µl) increased the size of the peak at 3.26 δ.

(b) 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5, 5-trimethoxy-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole. In this case, a saturated solution of the phosph(v)ole was used due to its low solubility. After only 4.5 min, there was only a small phosph(v)ole doublet at 4.80δ, and a significant product doublet at 5.58δ. There were also singlets at 4.00δ and 3.26δ. The reaction appeared to be complete within 15 min, the spectrum showing only one product doublet. Spiking with methanol (1 μl) increased the singlet at 3.26δ.

(c) 4, 5-Dihydro-5, 5, 5-trimethoxy-4-(4-methoxyphenyl)-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole. After the reaction was complete, the precipitate was filtered off and the $^{1}$H n.m.r. of the solution examined. This showed a very small doublet at 5.45δ and a very large peak at 3.26δ. This singlet increased in size on spiking with methanol (5 μl).

## O. Miscellaneous Experiments

### (1) Reaction of 2-(2-hydroxyphenyl)-1-nitroethene with diphenylphosphinous chloride.

This reaction was first carried out by Dr. P.K.G. Hodgson. The nitroethene (1.98 g; 12 mmol) was suspended in dry benzene (200 ml) and dry nitrogen passed into the mixture continuously. Some of the solid dissolved. The mixture was cooled briefly in an ice bath and diphenylphosphinous chloride (2.65 g; 12 mmol) added in a single portion. The passage of nitrogen was discontinued and the mixture stirred for 5 days, giving a red solution and a brown precipitate. The precipitate was filtered

off, and washed by refluxing in methylal (500 ml) for several hours giving an off-white solid (2.28 g; 49%), m.p. 161-163°C; $\nu_{max}$ 3340 (broad) (OH), 1632 (C=N), 1160 $cm^{-1}$; $\delta_H$ ($d_6$-DMSO): 5.91 (1H, d, $J_{PH}$ = 10 Hz, CH-P), 7.00-8.34 (14H, m, ArH), 10.13 (1H, broad s, removed by $D_2O$ shake, C=N.OH), 12.25 (1H, s, removed by $D_2O$ shake, phenolic OH H-bonded); $\delta_P$ (80% D.M.F. -20% $C_6D_6$): +28.6 p.p.m.; $\delta_C$ ($d_6$-DMSO): 155.2 (d, $J_{PC}$ = 6 Hz, C=N), 135.1-127.9, 118.8-115.4, 45.0 p.p.m. (d, $J_{PC}$ = 66 Hz, C-P); $\delta_C$ ($CDCl_3$+$CH_3OH$): 155.8 p.p.m. (Found: C, 62.6; H, 4.4; N, 3.6%. $C_{20}H_{17}ClNO_3P$ requires C, 62.3; H, 4.4; N, 3.6%). m/e 369 ($M^+$, 3.5%), 367 ($M^+$, 10), 349 (15), 333 (83), 202 (88), 201 (100), 121 (29), 120 (29).

(2) Photolysis of 2-oxo-1, 2, 5-oxazaphosph(v)oles

(a) 4, 5-Dihydro-5, 5-dimethoxy-4-(4-methylphenyl)-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole (1.02 g, 2.5 mmol) was dissolved in chloroform (400 ml) and the solution photolysed under nitrogen using a Phillips 15 W U.V. lamp and a falling curtain reactor. After 140 min, tlc showed no phosph(v)ole remaining. Removal of the solvent from the dull orange solution gave a brown oil which was shown by tlc to be a complex mixture of products. $^{31}P$ N.m.r. indicated the presence of dimethyl phenylphosphonate ($\delta_P$: +21.1 p.p.m.) in addition to a number of other P=O compounds.

(b) 4, 5-Dihydro-5, 5-dimethoxy-4-(4-methoxyphenyl)-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole (1.06 g; 2.5 mmol) was dissolved in chloroform (300 ml) and triethyl phosphite (0.87 ml; 5 mmol) added. The solution was photolysed under nitrogen using a 15W U.V. lamp and a falling curtain reactor. After 2.5 h, tlc showed no phosph(v)ole remaining. Evaporation

of the resultant brown solution gave a greenish-brown oil (2.28 g) which was shown by $^{31}$P n.m.r. to contain principally triethyl phosphate, dimethyl phenylphosphonate and two other P=O compounds. Tlc showed no spot corresponding to 6-methoxy-2-phenylindole. Lplc of the oil gave only small amounts of unidentified oils.

(3) Reaction of 4-(4-chlorophenyl)-4, 5-dihydro-5, 5, 5-trimethoxy-2-oxo-3-phenyl-1, 2, 5-oxazaphosph(v)ole with hexachlorodisilane.

The phosph(v)ole (0.075 g; 0.2 mmol) was dissolved in dry deuteriochloroform (0.3 ml) and a few drops of hexachlorodisilane added. The solution turned pale blue, then went green, then yellow. After 15 min, $^{31}$P n.m.r. showed no phosph(v)ole remaining, but showed a major peak at +21.9 p.p.m. and a minor peak at +20.3 p.p.m.

(4) Reaction of 2-(2-furyl)-1-phenylnitroethene with triethyl phosphite.

To the nitroethene (0.043 g; 0.2 mmol) in an n.m.r. tube was added tert-butanol (0.4 ml) and triethyl phosphite (0.087 ml; 0.5 mmol). The mixture was shaken under nitrogen and the reaction followed by $^{31}$P n.m.r. After 4 h, there was a large peak at +15.5 p.p.m. and a significant peak due to triethyl phosphate. There were also two peaks in the phosphorane region of the spectrum, one at -40.8 p.p.m. (major) and the other at -29.7 p.p.m. After 23 h, there were large peaks due to triethyl phosphate and at +15.5 p.p.m. There was also a significant peak at -29.6 p.p.m., but no peak at -40.8 p.p.m.

## Discussion

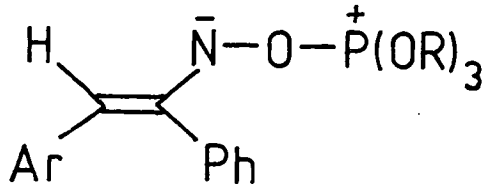
### A. Reaction of 2-Aryl-1-phenylnitroethenes with Tervalent Phosphorus Reagents.

#### A.1 High temperature deoxygenation of 2-aryl-1-phenylnitroethenes.

As indicated in the introduction, there appears to be essentially two types of reaction of tervalent phosphorus reagents with nitroethenes. The first of these is the high temperature reaction leading to total deoxygenation of the nitro group with resultant formation of nitrene-derived products.[17] The second of these leads to the formation of products where the phosphorus atom is attached to the carbon which was originally β to the nitro group. Such products include the 2-oxo-1,2,5-oxazaphosph(v)oles,[128,129,137] vinyl phosphonates,[131,133,215] and oxime phosphonates.[130,135,136] The latter reactions tend to predominate at low temperature. The aim of the present work was to investigate further the synthetic and mechanistic significance of these reactions, in particular those involving the 1,2,5-oxazaphosph(v)oles. This section will deal with the high temperature deoxygenation reaction.

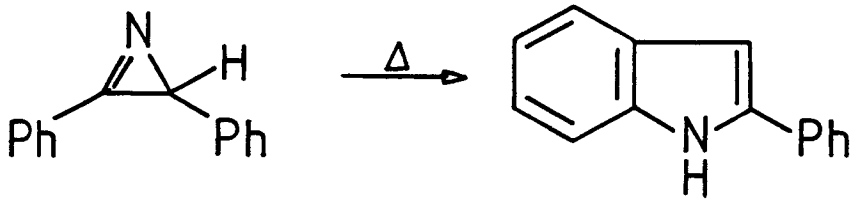
Although formally the deoxygenation products may be considered to arise from a nitrene, in most cases discussed here the alternative possibility of a nitrene precursor (46, for example) has not been excluded. For simplicity, however, the reactions will all be discussed in terms of nitrenes.

Cadogan and co-workers[17] demonstrated that E-1,2-diphenyl-



(46)

nitroethene (α-nitrostilbene) gives 2-phenylindole (16%) on deoxygenation with triethyl phosphite at 156°C. The possibility that this reaction proceeds *via* the nitrene gains support from the observation[216,217] that thermolysis of 2,3-diphenyl-2*H*-azirine gives 2-phenylindole in up to 75% yield (Scheme 87). Decomposition *via* the vinyl nitrene is

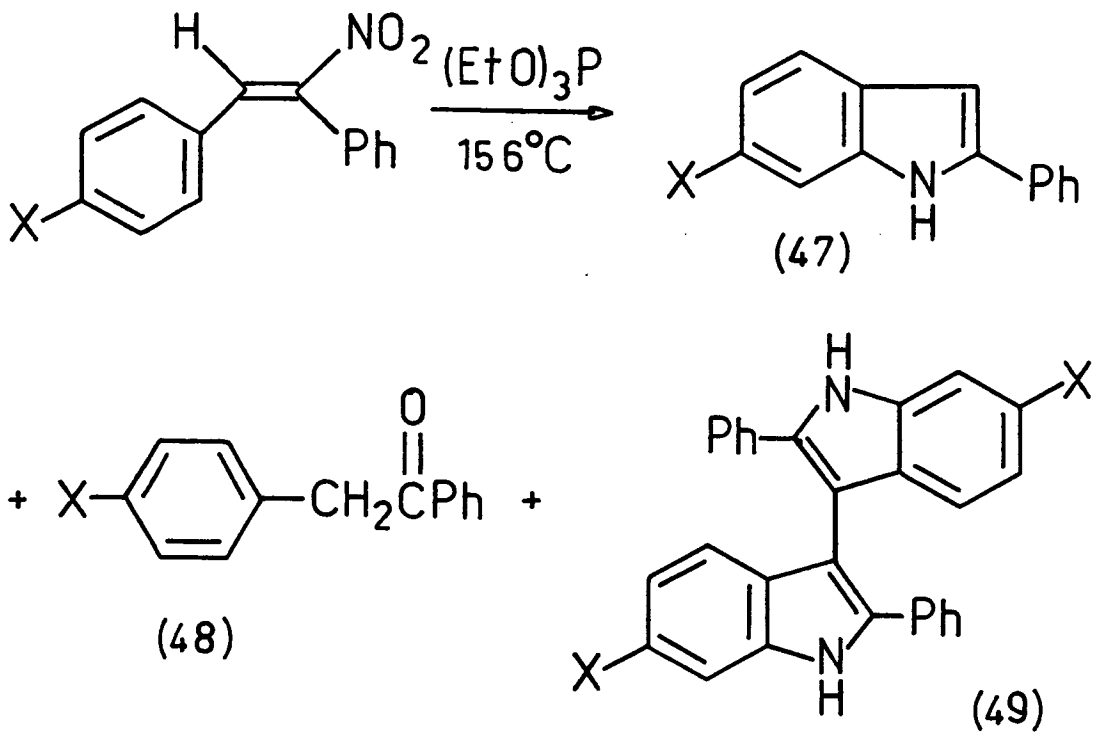


Scheme 87

recognised[216] as one of the major routes involved in the thermolysis of 2*H*-azirines. Indeed, it has been postulated[218] that the 2*H*-azirine and the vinyl nitrene exist in equilibrium. The involvement of carbenes has also been postulated[216] in azirine decompositions. The 2*H*-azirines are themselves prepared by photolysis[219-221] or thermolysis[220-224] of vinyl azides. Although no 2*H*-azirines were detected in the deoxygenation reactions described here, their possible intermediacy provides a solution to the problem of the low yields obtained, because it is known that 2*H*-azirines are prone to polymerisation.[225]

In order to investigate further the deoxygenation of 2-aryl-1-phenylnitroethenes, a series of these substituted in the 4-position of

the aryl ring was prepared by the method of Robertson.[193] These were then reacted with a two-fold excess of triethyl phosphite, with or without added solvent, and the products isolated by low pressure liquid chromatography. In each case, up to three products were obtained. These were the 6-substituted-2-phenylindole (47), the 2-(4-substituted-phenyl)-1-phenylethan-1-one (48), and the 6,6'-disubstituted-2,2'-diphenyl-3,3'-biindolyl (49) (Scheme 88). In one case ($X=CH_3$), a low




Scheme 88

yield of 3,5-diphenyl-4-(4-methylphenyl)isoxazole was obtained. This was not a true product, however, but merely an impurity present in the reactant nitroethene.[193] The yields of these products obtained in each case are tabulated in Table 4.

Table 4

Products from high temperature deoxygenation of 2-aryl-1-phenylnitroethenes.

| | Product yield (%) | | |
|---|---|---|---|
| X | (47) | (48) | (49) |
| $CH_3O$ [a] | 7 | 5 | 14 |
| $CH_3O$ [b] | 5 | ca 1 | 17 |
| $CH_3O$ [c] | 1.2 | - | 14 |
| $CH_3O$ [d] | 9 | 4 | 16 |
| $CH_3$ [a] | 15 | 4.4 | - |
| Cl [a] | 12 | 3.3 | - |

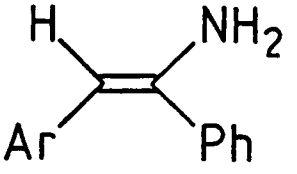
(a) In the presence of neat triethyl phosphite.

(b) In 1,2,3-trichlorobenzene as solvent.

(c) In benzene as solvent.

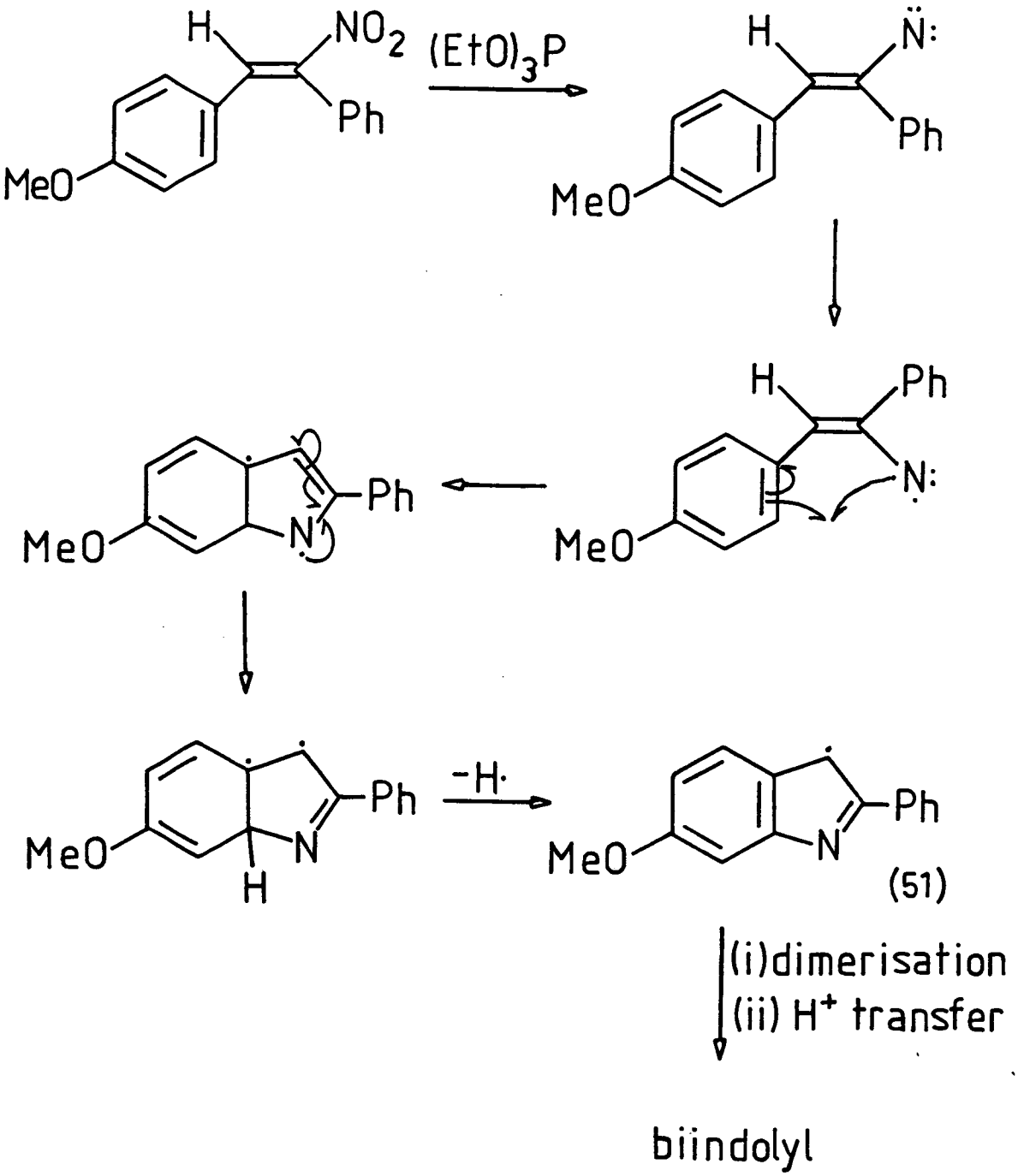
(d) In triethyl phosphite with 6% added 6-methoxy-2-phenylindole.

The formation of the indole is expected as a result of nitrene insertion into a C-H bond of the aryl ring. The formation of the ketone (48) can be rationalised in terms of another reaction of nitrenes, namely abstraction. Abstraction of two hydrogen atoms from the solvent by the vinyl nitrene would result in the formation of an enamine (50), which




(50)

would hydrolyse to the ketone on work-up on silica. The genesis of the biindolyl is less obvious, but one can postulate a mechanism for its formation (Scheme 89) similar to that proposed by Cadogan[2] for formation of biindoline from deoxygenation of β,β-disubstituted o-nitrostyrenes.




Scheme 89

The first step involves total deoxygenation of the nitro group to give the singlet nitrene which then undergoes intersystem crossing (ISC) to the triplet. A double bond isomerisation has been included in the ISC step although it need not necessarily occur at this stage. The triplet nitrene then cyclises on to the aryl ring, followed by an electron shift and loss of a hydrogen atom leading to (51). Dimerisation of (51) followed by proton transfer to the nitrogen then leads to the biindolyl.

To test if the biindolyl was formed from the indole, the deoxygenation of 2-(4-methoxyphenyl)-1-phenylnitroethene was carried out in the presence of 6% added indole (this percentage is based on the theoretical yield of indole obtainable from the deoxygenation reaction). It can be seen from the table that the yield of indole obtained (9%) is smaller than would have been expected (13%) if the added indole was not consumed in the reaction. In addition, there is a small increase in the yield of biindolyl. Although the differences are too small for conclusions to be drawn with any great certainty, it does appear that the indole is reacting with some intermediate formed in the reaction and is thereby being converted to the biindolyl. A possible candidate is the indolyl radical (51) which might be expected to react with the indole molecule at the reactive 3-position to give the dimer, in the same way that phenyl radicals react with benzene to give biphenyl.[226] It is not clear why the biindolyl is not formed when $X=CH_3$ or Cl.

Since all the nitroethenes which were synthesised were found by examination of their U. V. spectra to have the E-configuration,[194] it is clear that at some stage in the formation of the indoles and the biindolyl, a double bond isomerisation (or its equivalent) must take place. If this

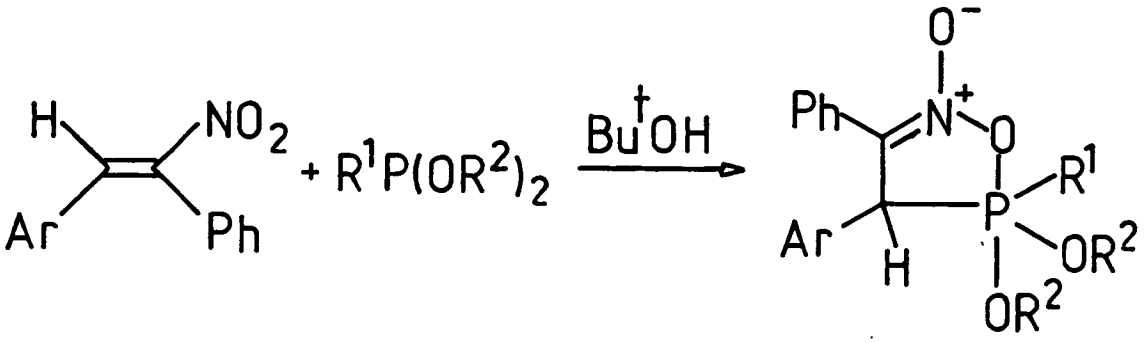
is the case, then higher reaction temperatures should increase the rate of isomerisation and so favour the formation of insertion products. A deoxygenation reaction carried out in 1,2,3-trichlorobenzene at 212°C failed to show this conclusively, however. In fact, the yield of indole was reduced although there was a small increase in the yield of biindolyl. An increased yield of the biindolyl would be expected on other grounds in addition to the isomerisation argument. If the biindolyl is formed exclusively from the triplet nitrene, then an increase in collisional intersystem crossing from singlet to triplet, due to an increase in temperature, would increase the yield. The reduced yield of indole may be due to diversion of the nitrene to the biindolyl or to thermal decomposition at this temperature. Lowering the temperature by performing the reaction in benzene produced the expected lowering of the indole yield to ca 1%. In this case, it is the yield of biindolyl which is anomalous, being exactly the same as that at 156°C. In addition to the above observations, it has previously been reported[195] that deoxygenation of Z-1,2-diphenylnitroethene gives 2-phenylindole in only 8% yield compared with 16% from the corresponding E-isomer.

In conclusion, it appears that a simple double bond isomerisation of either the nitroethene or the vinyl nitrene is not sufficient to account for the observed formation of indole derivatives. As will be shown in the following section, this problem can be overcome by considering alternative routes to the vinyl nitrene. The low yields of non-phosphorus-containing products in the above reactions can be accounted for by invoking the intermediacy of a 2H-azirine which can polymerise, and by formation

of highly polar phosphorus-containing products which would be strongly adsorbed by the silica used in the chromatographic work-up. The origin of the phosphorus products will also be dealt with in the following section.

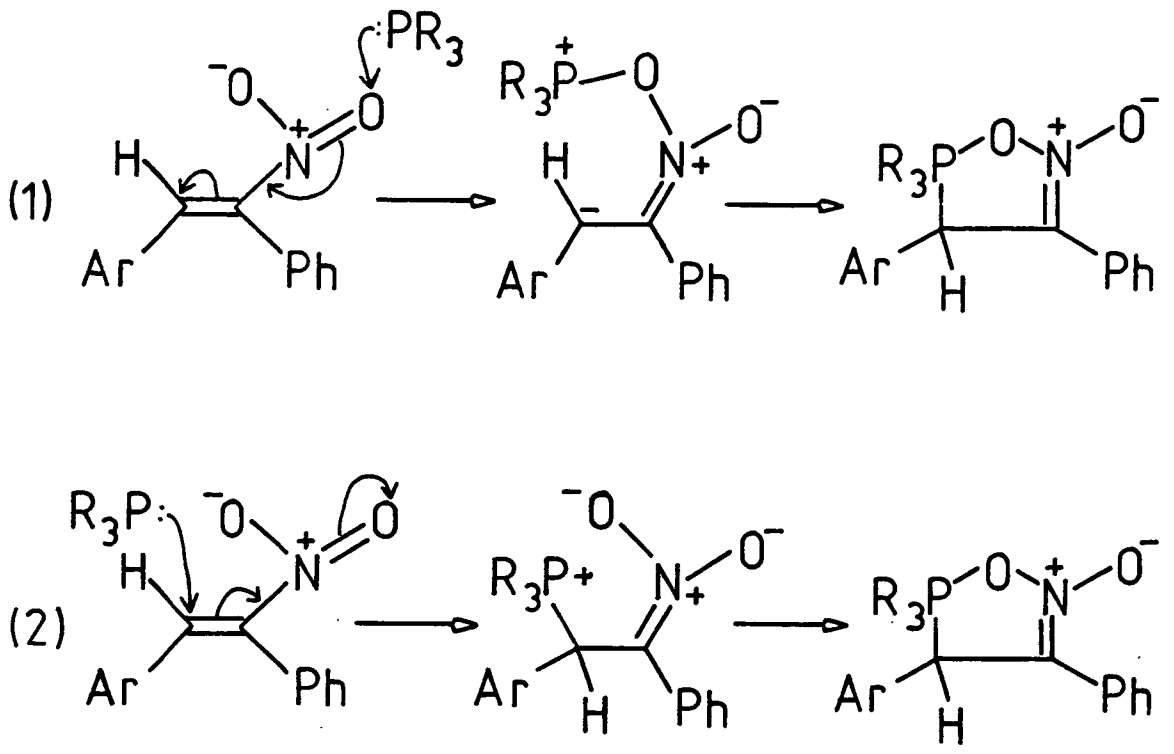
A. 2 Formation of 2-oxo-1, 2, 5-oxazaphosph(v)oles

Gareev and his co-workers[128-135, 215] showed that an alternative low temperature pathway existed for the reaction of nitroethenes with tervalent phosphorus reagents. This resulted in the formation of products with the phosphorus attached to the carbon originally β to the nitro group. Among the products obtained were the 2-oxo-1, 2, 5-oxazaphosph(v)oles, although these were unstable and inadequately characterised. These phospholes have also been postulated as intermediates in a number of reactions.[140, 141] More recently, the corresponding 3, 4-diaryl-4, 5-dihydro-2-oxo-1, 2, 5-oxazaphosph(v)oles, which are stable, have been prepared,[137] by reaction of 2-aryl-1-phenylnitroethenes with tervalent phosphorus reagents in t-butanol at room temperature (Scheme 90), and characterised.




Scheme 90

There are three possible mechanisms of formation of these phospholes (Scheme 91). Mechanism (1) involves conventional attack of the



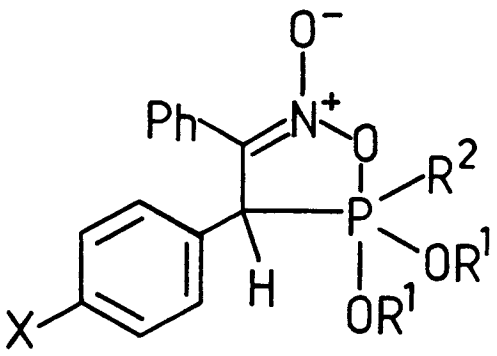

Scheme 91

phosphorus reagent at the nitro group to give the dipolar ion which then cyclises. Route (2) involves Michael attack at the β-position of the double bond followed by cyclisation. The third possibility is concerted 1,4-addition to the α,β-unsaturated nitro system, and is an example of a chelotropic reaction. Although there is no concrete evidence to suggest which mechanism is operative, either route (2) or (3) involving carbon attack would seem the most likely in view of the powerful electron-withdrawing character of the nitro group.[227] The nature of the other products arising from the low temperature reaction of nitroethenes with phosphorus(III) reagents would tend to support this conclusion.

In this investigation, a series of 2-oxo-1,2,5-oxazaphosph(v)oles was prepared in order to investigate the role of these phospholes in the nitro/phosphite reaction. Some representative examples of the phospholes prepared are given in Table 5. The phospholes were prepared

Table 5

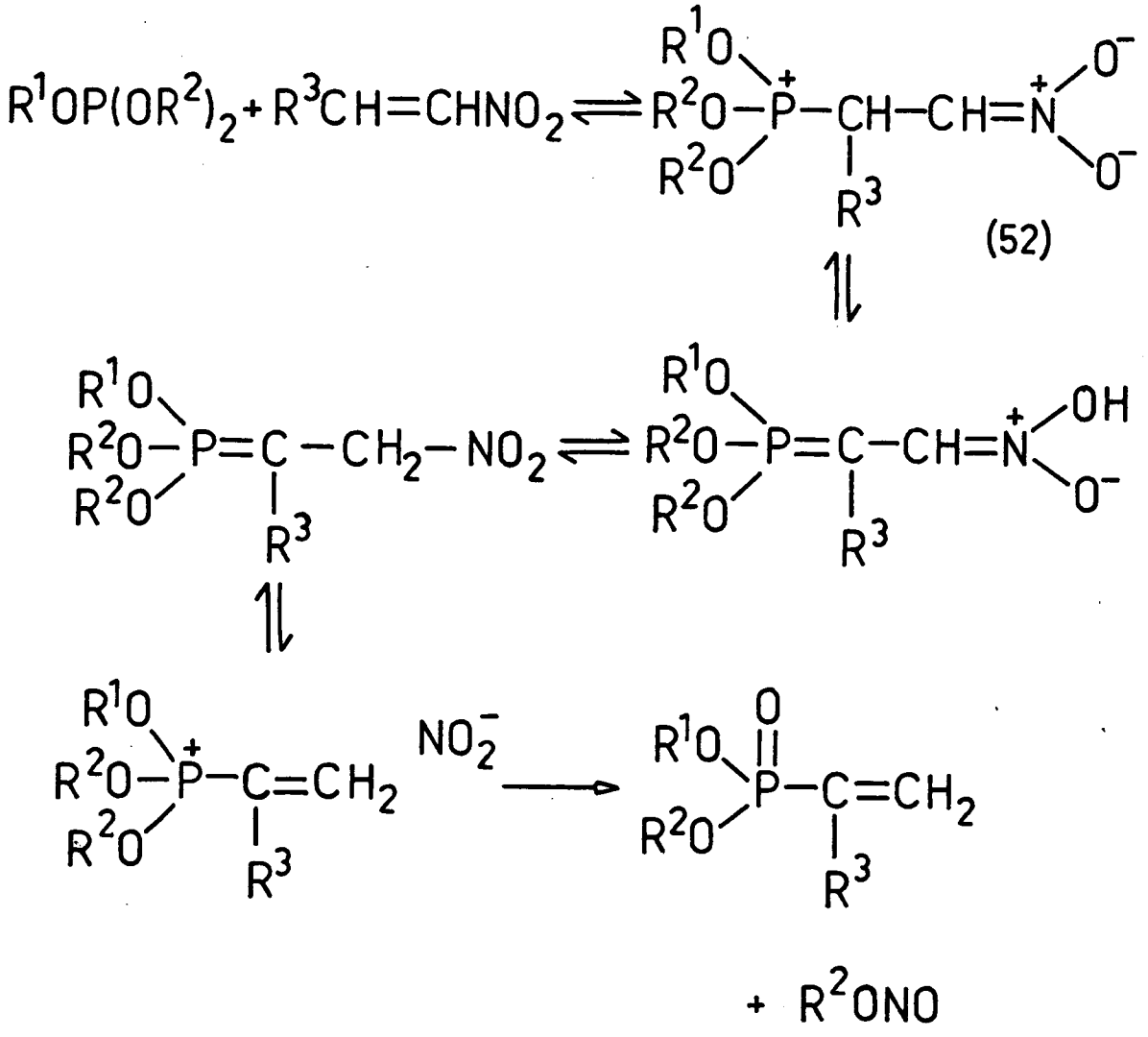
3,4-Diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(v)oles



| $R^1$ | $R^2$ | X | Yield (%) |
|---|---|---|---|
| $CH_3$ | $OCH_3$ | $OCH_3$ | 79 |
| $CH_3$ | $OCH_3$ | Cl | 88 |
| $C_2H_5$ | $OC_2H_5$ | $CH_3$ | 80 |
| $C_2H_5$ | $OC_2H_5$ | Cl | 47 |
| $CH_3$ | Ph | $OCH_3$ | 97 |
| $CH_3$ | Ph | $CH_3$ | 98 |

from trimethyl phosphite, triethyl phosphite, and dimethyl phenylphosphonite. The yields obtained are in general very high and, indeed, are probably quantitative, all losses being purely handling losses. This is supported by $^{31}P$ n.m.r. observations. The phospholes prepared

from trimethyl phosphite and dimethyl phenylphosphonite were insoluble in t-butanol and so could be isolated easily. In the case of triethyl phosphite, the resultant phospholes were sometimes soluble, making isolation more difficult and occasionally resulting in low yields. All the phospholes were found to be stable when stored under nitrogen at -20°C. The rates of formation of the phospholes are probably governed to a large extent by the solubility of the reactant nitroethene in the solvent t-butanol. The failure to form the phosphole when the aryl ring of the nitroethene contains a p-electron-withdrawing group is of interest because it is consistent with the mechanism proposed by Gareev and co-workers[215] for the formation of vinyl phosphonates (Scheme 92).



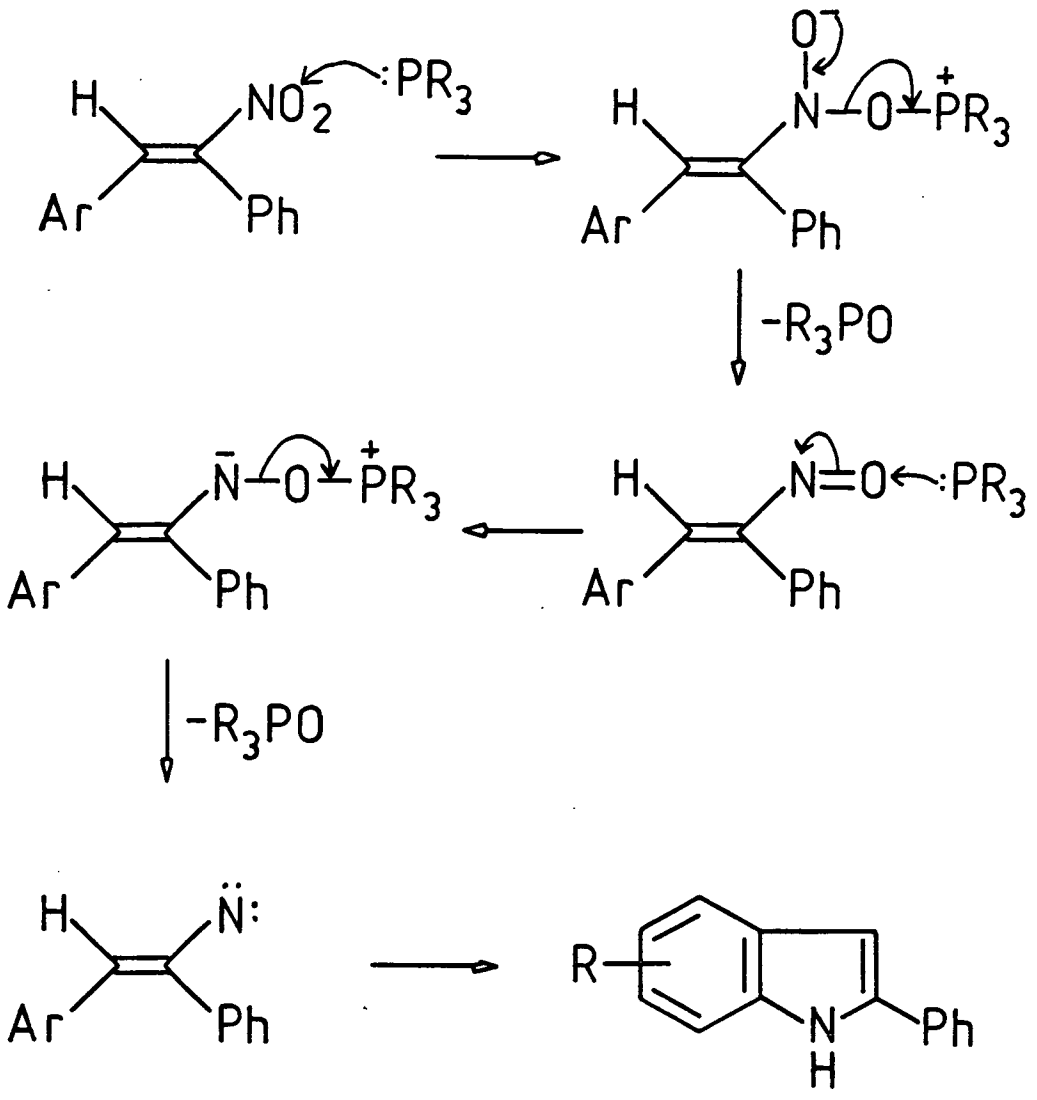
Scheme 92

If the dipolar ion (52) cyclises, then the oxazaphosphole is formed. If $R^3$ is a strongly electron-withdrawing group such as p-cyanophenyl- or p-nitrophenyl-, then the ylidic intermediates will be stabilised and this will tend to divert the reaction from phosphole formation towards the vinyl phosphonate. The red or orange colour observed in some of these reactions could also be attributed to the formation of ylidic species. This therefore provides a satisfactory explanation for the failure to prepare the p-cyano and p-nitro phospholes. At first sight, the previous isolation[137] of a phosphole from the reaction of 2-(2-nitrophenyl)-1-phenylnitroethene with trimethyl phosphite would appear to contradict this, but in this case steric factors must also be taken into account. The nitro group is a sterically bulky group and in the o-position of the phenyl ring it will hinder coplanarity of the aryl ring with the ylide double bond and thus prevent the full electronic effect of the nitro group being experienced.

The characteristic spectroscopic data for the 2-oxo-1,2,5-oxazaphosph(v)oles will be discussed in Section B. 1.

## A. 3 Intermediacy of the 2-oxo-1,2,5-oxazaphosph(v)oles

The possibility that these phospholes might be intermediates in the high temperature reaction of 2-aryl-1-phenylnitroethenes with phosphorus(III) reagents was considered. If this was found to be the case, it would have important consequences for the mechanism of the deoxygenation reaction, at least in the case of nitroalkenes. Scheme 93 shows the generally accepted mechanism[17] for the formation of indole from the nitroethenes. Although oxygen attack at the nitro group



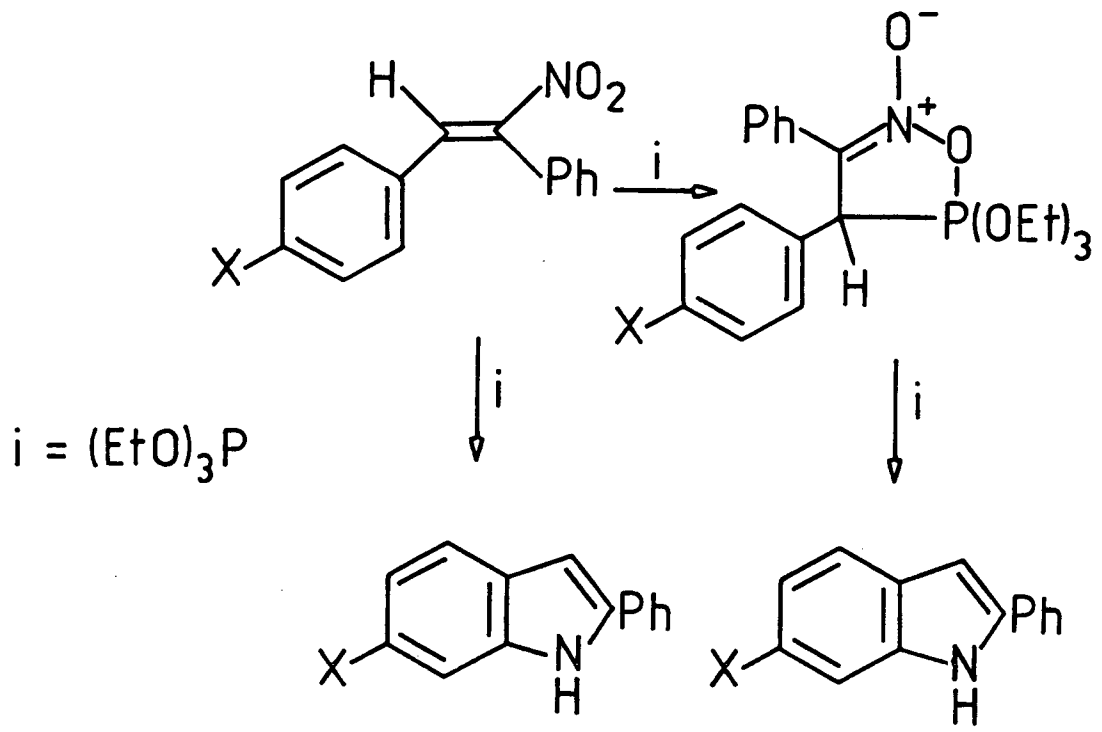
Scheme 93

has been shown, initial nitrogen attack could also be considered. The reaction is assumed to proceed via the nitrosoethene, but none has ever been isolated since the nitroso group would deoxygenate so much faster than the nitro group under the reaction conditions. There has in fact been no satisfactory demonstration of nitroso group intermediacy in any deoxygenation reaction to date. Stepwise deoxygenation of the nitro group leads finally to the vinyl nitrene which then cyclises to the indole. As mentioned in section A. 1, at some stage in the mechanism, a double bond isomerisation must occur.

Peaks in the $^{31}P$ n. m. r. spectrum due to the 2-oxo-1,2,5-oxazaphosph(v)oles have previously been observed[195] in the deoxygenation of 1,2-diarylnitroethenes in $d_6$-benzene at 78°C. The spectra show the formation and subsequent decomposition of the phosphole during the course of the reaction. It has already been shown, however, that at this temperature the yield of indole is low and so these observations do not constitute proof that the phospholes are intermediates in the high temperature (156°C) reaction. In order to demonstrate that this was the case, it was considered necessary to show that high temperature deoxygenation of the phospholes led to essentially the same products as the nitroethene deoxygenation reactions. The technique used to effect the deoxygenation was one of dripping a solution of the phosphole in triethyl phosphite into boiling triethyl phosphite. The reason for this was to mimic the situation expected to occur in the nitroethene deoxygenation reaction, in which at any time the concentration of the phosphole might be expected to be low and fairly constant (steady state approximation). The results of the deoxygenations are shown in Table 6. Triethyl phosphite was used as the deoxygenating agent because it is known to lead to cleaner reactions than trimethyl phosphite in nitro deoxygenations. It can be seen from the results that comparable yields of 6-substituted-2-phenylindoles are obtained from the two deoxygenation reactions. This is considered to be good evidence for the intermediacy of the phospholes in the high temperature deoxygenation of the nitroethenes. When X=Cl, 1% of 2-(4-chlorophenyl)-1-phenylethan-1-one was also isolated. When $X=CH_3O$, a much higher yield of indole was obtained from the phosphole deoxygenation

Table 6

Comparison of deoxygenation of 2-oxo-1,2,5-oxazaphosph(v)oles and 2-aryl-1-phenylnitroethenes.



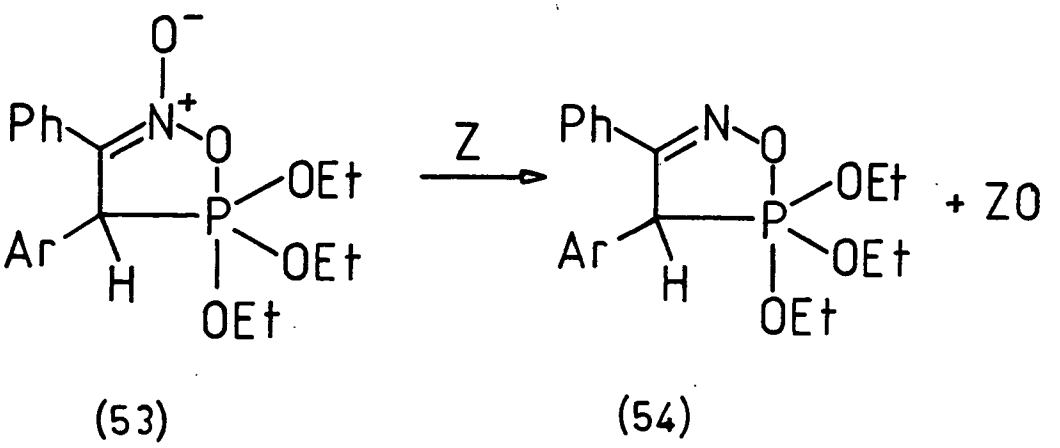

| X | Yield (%) | Yield (%) |
|---|---|---|
| H | 16 [17] | 12 |
| $CH_3O$ | 7 | 18 |
| $CH_3$ | 15 | 12 |
| Cl | 12 | 7 |

than from the nitroethene, and, additionally, only a trace of the biindolyl was detected by tlc. This suggests that the formation of the phosphole is not the only route available to the reaction, and that the biindolyl arises by an alternative pathway. There is no evidence to indicate

what this pathway might be, however. In the case of $X=CH_3$, another deoxygenating procedure was also employed. This involved heating a solution of the phosphole in triethyl phosphite to reflux and heating under reflux for 18 h. This resulted in a drop in the yield of indole from 12% to 5.6%, most probably due to phosphole decomposition accompanying the deoxygenation. This result confirms the usefulness of the drip-in technique as a more accurate model of the true reaction conditions.

North[195] studied the reaction of a 2-oxo-1,2,5-oxazaphosph(v)ole with trimethyl phosphite by $^{31}P$ n.m.r. and observed the formation of an intermediate compound with a chemical shift of -25.5 p.p.m. Compounds with similar shifts were also observed in some deoxygenation reactions of 1,2-diarylnitroethenes. The negative value of the chemical shift suggests that the compound is another pentacoordinate phosph(v)ole, and it seems reasonable to assume that the N-oxide function of the 2-oxo-1,2,5-oxazaphosph(v)ole has been deoxygenated. A series of $^{31}P$ n.m.r. experiments was carried out in order to investigate the possibility of converting the 2-oxo-1,2,5-oxazaphosph(v)oles (53) exclusively to the 1,2,5-oxazaphosph(v)ole (54) (Scheme 94).* When the aryl group was 4-methoxyphenyl, reaction with triethyl phosphite led to the formation of the oxazaphosphole with simultaneous formation of triethyl phosphate. With increasing time, the oxazaphosphole peak increased in intensity relative to the oxazaphosphole oxide, but the intensity of the triethyl phosphate peak increased even more rapidly. As the triethyl phosphate peak continued to increase in intensity, so that due to the oxazaphosphole

* From this point onwards, the 2-oxo-1,2,5-oxazaphosph(v)oles will be referred to as 'oxazaphosphole oxides,' and the deoxygenated 1,2,5-oxazaphosph(v)oles as 'oxazaphospholes.'



(53) (54)

Scheme 94

began to diminish. It appears from these results that as the oxazaphosphole is being formed, some of it is thermally decomposing with loss of triethyl phosphate. Methyl diphenylphosphinite is a much more reactive deoxygenating agent towards nitro groups than triethyl phosphite, but it did not react with the oxazaphosphole oxide at room temperature. On increasing the temperature, reaction took place but the product oxazaphosphole again tended to decompose. When the aryl group was 4-chlorophenyl and 4-methylphenyl, reaction conditions were found whereby the oxazaphosphole appeared to be formed almost exclusively, with only a few small peaks in the P=O region of the spectrum. When the aryl group was 2,4,6-trimethoxyphenyl or 2,4,6-trimethylphenyl, the conversion to the oxazaphosphole appeared to be quantitative after 60s at 150°C and 30s at 154°C respectively in triethyl phosphite. The precise reaction conditions required for the above conversions were quite critical if decomposition of the product oxazaphosphole was to be avoided.

In the sphere of non-phosphorus-containing deoxygenating agents,

it has been reported that hexachlorodisilane is a very mild reagent for the reduction of nitrones and similar N-oxides in high yield.[228] As the oxazaphosphole oxides are themselves N-oxides, one of these was reacted with hexachlorodisilane in deuteriochloroform. Unfortunately, $^{31}$P n. m. r. showed no oxazaphosphole but exhibited peaks in the same position as those arising from reaction of the oxazaphosphole oxide with hydrochloric acid. From this, it would appear that the oxazaphosphole oxide has simply reacted with hydrogen chloride present as a hydrolysis impurity in the hexachlorodisilane.

The above reactions were then attempted on a preparative scale.

Ar = 2,4,6-Trimethoxyphenyl. The oxazaphosphole oxide reacted with triethyl phosphite in 60s at 150°C, giving a crystalline solid after removal of the solvent. After washing, the oxazaphosphole was obtained as nearly white crystals in 50% yield.

Ar = 2,4,6-Trimethylphenyl. The oxazaphosphole oxide reacted with triethyl phosphite in 90s at 162°C, giving an oil after removal of the solvent. The oil was triturated with water to remove triethyl phosphate and worked up to give the oxazaphosphole as colourless crystals in 42% yield.

The structure of the oxazaphospholes (54) was confirmed by examination of their spectroscopic data. Both showed characteristic negative $^{31}$P n.m.r. shifts at ca -26 p. p. m. This confirms the assignments made in the n. m. r. experiments. The proton n. m. r. spectra both exhibited a large doublet due to a solitary proton on a carbon attached to the phosphorus atom. In both compounds, the m-protons in the aryl ring were non-equivalent, as were the o-aryl methoxyl and

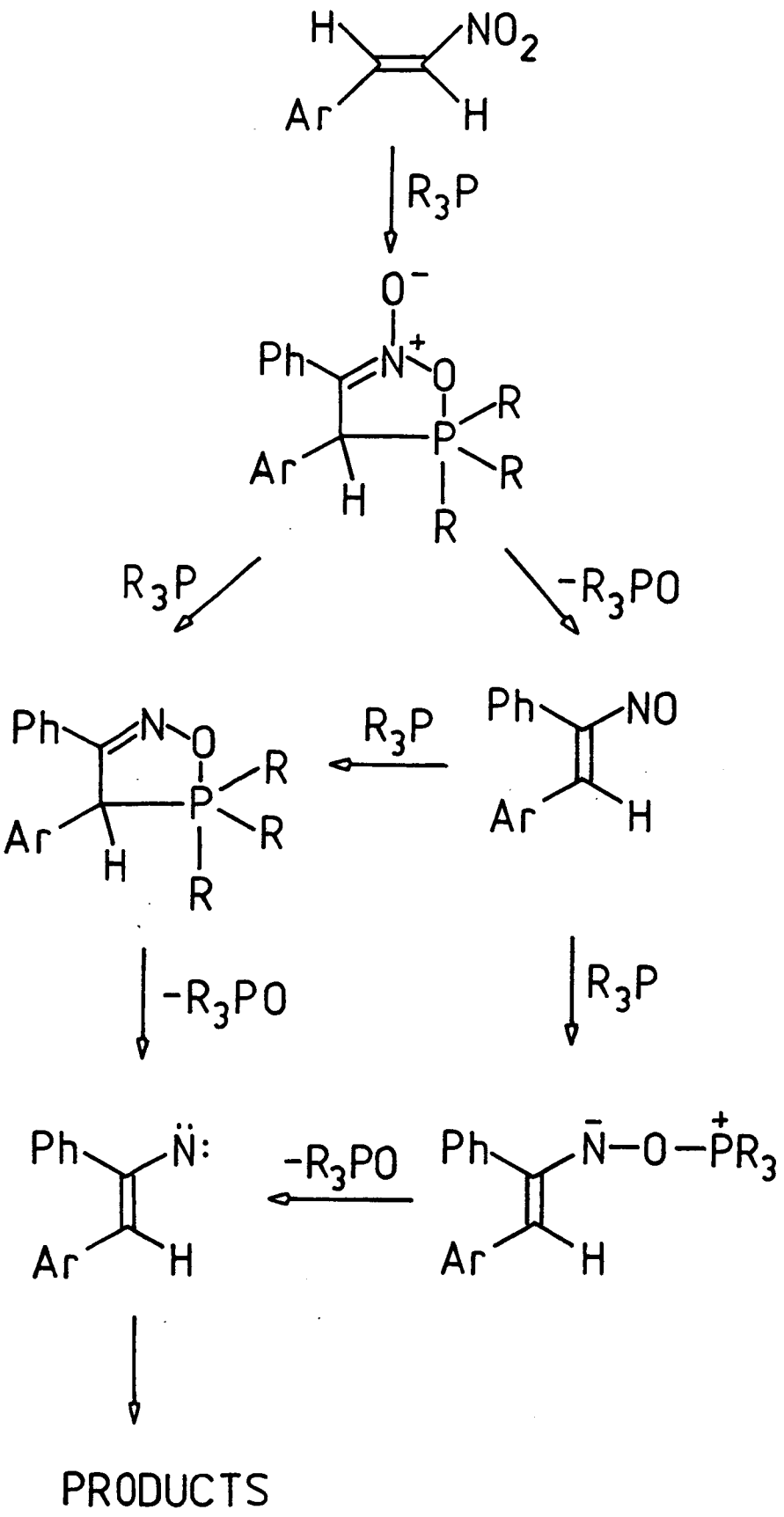
methyl protons. This is indicative of hindered rotation of the aryl ring about the bond connecting it to the oxazaphosphole ring. The variable temperature n. m. r. spectrum of one of the oxazaphospholes is discussed later. Both spectra exhibited a downfield aromatic group of signals which is attributable to the o-protons in the phenyl ring attached to the C=N grouping. The I. R. spectra of both compounds showed a group of peaks between 1050 and 1115 $cm^{-1}$, attributable to the P-O-C grouping. The spectrum of one also had two absorptions near 1600 $cm^{-1}$ which could be assigned to the C=N functionality. In both cases, the parent ion in the mass spectrum was weak and the base peak was due loss of ethanol. There were also prominent peaks due to loss of $(C_2H_5O)_3POH$.

The oxazaphosphole ring system to which these compounds belong is by no means new, but these are the first examples of this system where the groups attached to the phosphorus atom are alkoxy groups. Previous examples of the ring system have been prepared by the cycloaddition reaction of a nitrile oxide to an ylide[159-162] under necessarily basic conditions, or alternatively by base catalysed cyclisation of 2-oximinophosphonium salts.[163,164] Neither of these routes would seem feasible for the preparation of the above compounds, however, because of the likelihood of an Arbusov reaction occurring under the basic conditions used.

It is significant that in the examples discussed above, the aryl ring in both cases contained o-substituents, and in both cases the oxazaphosphole could be isolated in a pure form and $^{31}P$ n. m. r. suggested the reactions were quantitative. Problems arose when it

was attempted to isolate oxazaphospholes without o-substituents in the aryl ring. $^{31}$P N. m. r. (above) had already shown that the deoxygenation reactions were not as clean as those with o-blocking groups, but the situation still appeared reasonably promising. In practice, however, the preparative scale deoxygenations were inconsistent, with different results being obtained under identical reaction conditions. Isolation of the oxazaphosphole with a 4-chlorophenyl group proved to be impossible, and although a white solid was obtained when the aryl group was 4-methylphenyl, $^{31}$P n. m. r. indicated that it contained only about 80% of the required oxazaphosphole. It would appear from these results that oxazaphospholes without o-substituents in the aryl ring are much less thermally stable than those which have such substituents.

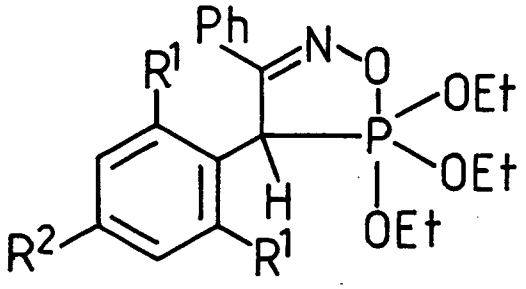
The isolation of these oxazaphospholes is significant as it suggests the possibility of an alternative to the generally accepted deoxygenation mechanism, at least in the case of nitroethenes (Scheme 95). The first step is the formation of the oxazaphosphole oxides, and it has already been shown that there is a high probability that these are intermediates in the deoxygenation reaction. Two possible routes from the oxazaphosphole oxides are then envisaged. The first involves deoxygenation of the oxide to give the oxazaphosphole and the second loss of the oxygenated phosphorus reagent to give the nitrosoalkene. The nitrosoalkene could then undergo a conventional type of deoxygenation to the nitrene, or it could undergo a Michael type addition akin to that done by the nitroalkene and so give the oxazaphosphole. Extrusion of the oxygenated phosphorus reagent from the oxazaphosphole could also


H
NO2
Ar
H
R3P
O−
Ph
N+
O
R
P
R
Ar
H
R
R3P
-R3PO
Ph
N
O
R
P
R
Ar
H
R
R3P
Ph
NO
Ar
H
-R3PO
R3P
Ph
N:
Ar
H
-R3PO
Ph
N̄—O—P̄R3
Ar
H
PRODUCTS

Scheme 95

lead to the nitrene, which would then go on to give the final products. Various aspects of this mechanistic scheme will be considered in turn.

The first part of the scheme which was investigated was the formation of a nitrene *via* elimination of triethyl phosphate from the oxazaphosphole. Thermolysis of oxazaphospholes to give products derived from a nitrene or nitrenoid species is not without precedent,[159-161] and the results described here provide additional support for this conclusion. The oxazaphospholes which were thermolysed were (54a-c).




(a) $R^1 = R^2 = MeO$

(b) $R^1 = R^2 = Me$

(c) $R^1 = H$ ; $R^2 = Me$

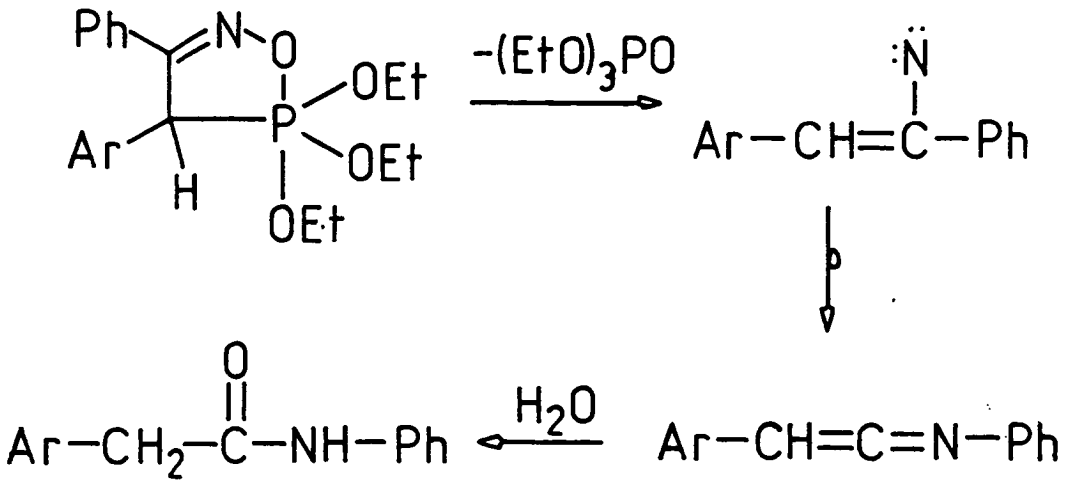
(54)

(54a) This was subjected to flash vacuum pyrolysis for 2 h at a furnace temperature of 500°C. The pyrolysis was not particularly clean, although a clear liquid pyrolysate identified as triethyl phosphate was obtained. $^1$H N.m.r. using a cyclohexane calibrant showed the yield to be 60%. No other products could be identified.

Thermolysis of the solid oxazaphosphole in a Kugelrohr apparatus showed the solid to be remarkably thermally stable. Total thermal decomposition gave triethyl phosphate (33%) as the only identifiable product.

The above techniques are obviously not suitable methods for thermolysing the oxazaphosphole. A solution thermolysis was attempted by dripping a solution of the oxazaphosphole in t-butylbenzene into

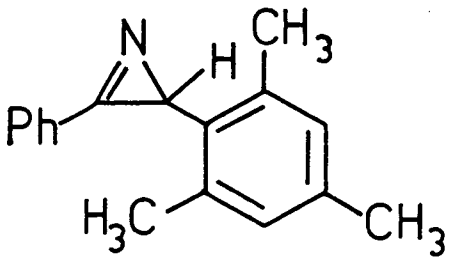
refluxing t-butylbenzene. $^{31}$P N. m. r. showed 100% extrusion of triethyl phosphate, and chromatographic work-up gave only one product identified as N-phenyl-2-(2,4,6-trimethoxyphenyl)acetamide (9%). The formation of the acetamide may be rationalised by the mechanism shown in Scheme 96. The phenyl migration is analogous to the Curtius




Scheme 96

rearrangement, and ketenimines have been observed in the pyrolysis[223] and photolysis[219] of vinyl azides. The loss of triethyl phosphate and the phenyl migration could be concerted and need not involve a discrete nitrene. Work-up of the reaction mixture on silica would lead to hydrolysis of the ketenimine, resulting in the formation of the acetamide.

(54b) Solution thermolysis of this oxazaphosphole led to only ca 60% extrusion of triethyl phosphate. Chromatographic work-up of the reaction mixture gave two products. One was a solid which was identified as the corresponding acetamide (12%) (cf. Scheme 96), and the other an oil identified as 2-(2,4,6-trimethylphenyl)-3-phenyl-2H-azirine (55) (14%). The spectroscopic data leading to this assignment is as

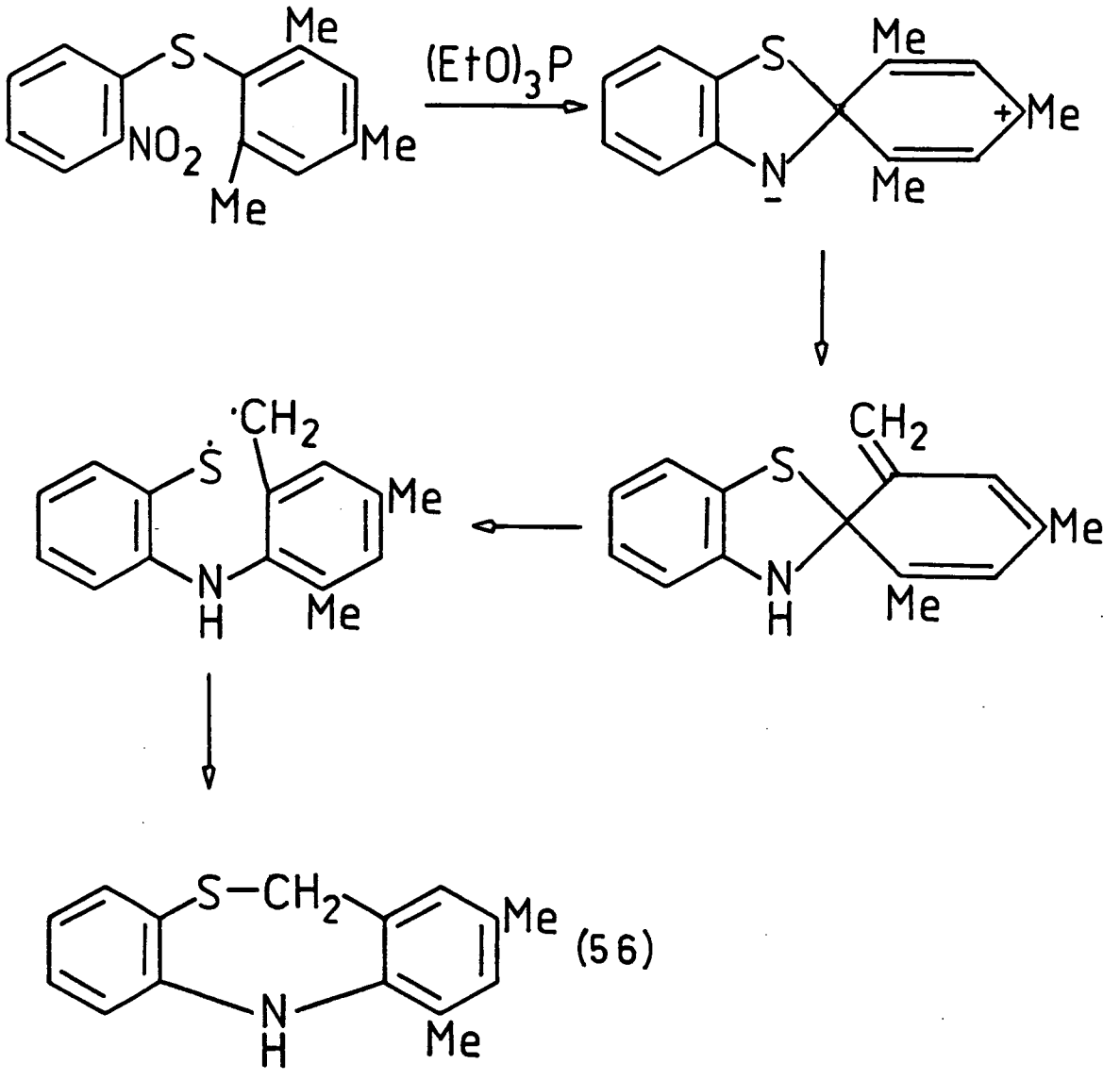


(55)

follows. The I. R. spectrum shows an absorption at 1738 $cm^{-1}$ which is characteristic of the azirine C=N.[161] The $^{1}H$ n. m. r. exhibits a singlet at 3. 29 δ due to the azirine ring hydrogen, and a downfield group of aromatic signals attributable to the o-protons in the phenyl ring attached to the C=N functionality. The C=N carbon appears in the $^{13}C$ n. m. r. spectrum at 169. 9 p. p. m. The parent ion is the base peak in the mass spectrum, and there is also a large peak due to loss of benzonitrile.

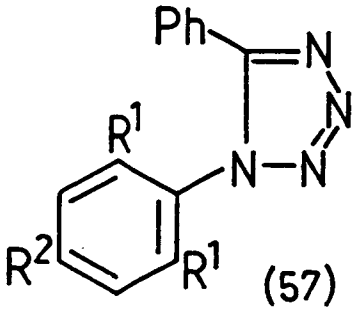
The isolation of the azirine is of particular significance because it has already been mentioned that 2H-azirines tend to decompose *via* the vinyl nitrene and that the two may exist in equilibrium. This therefore constitutes excellent evidence that the thermal decomposition of the oxazaphospholes proceeds *via* the vinyl nitrene, which can cyclise to give the 2H-azirine.

It is somewhat disappointing that the presence of the o-blocking groups in the oxazaphospholes did not lead to interesting nitrene-induced rearrangements. Cadogan and his co-workers[65] have observed a series of novel rearrangements in deoxygenation reactions of 2, 6-disubstituted aryl 2-nitrophenyl sulphides. For example, one of the products of the deoxygenation of 2, 4, 6-trimethylphenyl 2-nitrophenyl sulphide was the thiazepine (56) in 12% yield (Scheme 97). In this case, the o-blocking

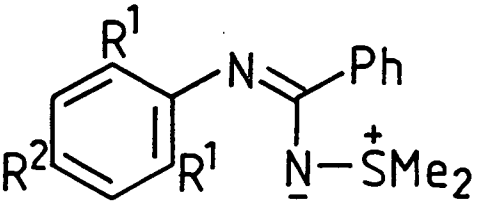



Scheme 97

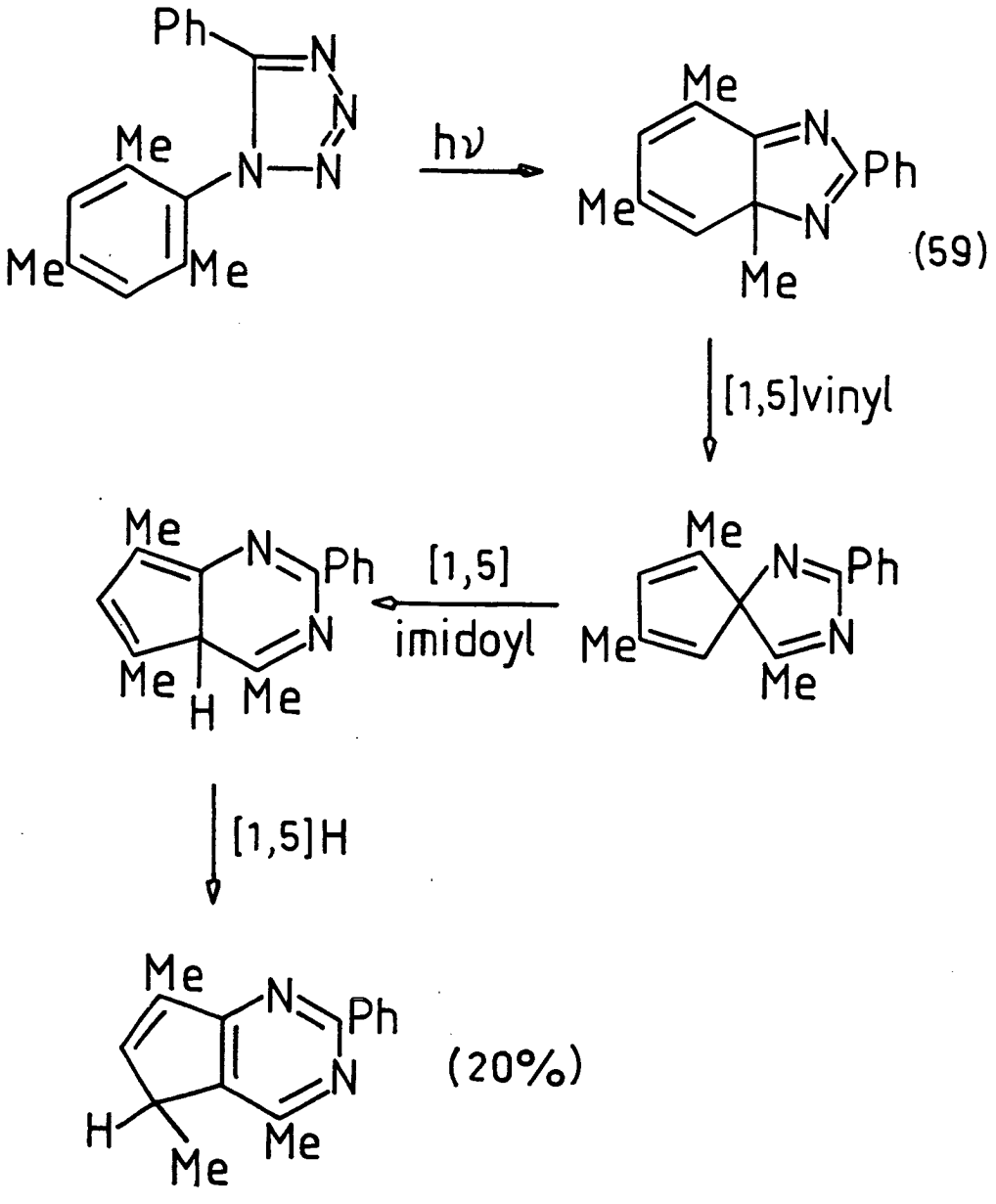
group is directly involved in the reaction. In a similar way, Rees and co-workers[229] obtained interesting products such as benzimidazoles and pyrimidines by photolysis and thermolysis of tetrazoles (57) and photolysis of sulphimides (58) with o-blocking groups (Scheme 98, for




(57)




(58)

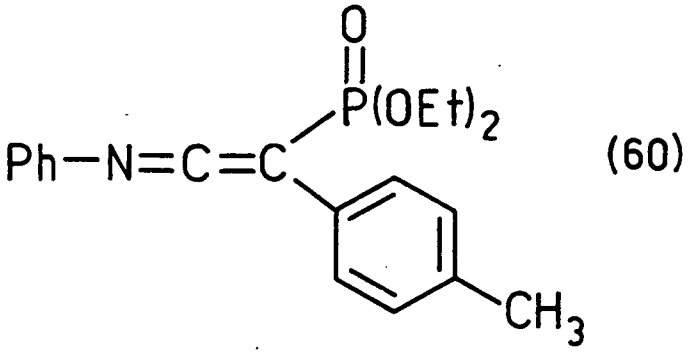



Scheme 98

example). The reaction is thought to proceed via the formation of an N-arylbenzimidoyl nitrene which ring closes to a 3aH-benzimidazole (59) which then proceeds via a series of [1,5] sigmatropic shifts to the products. Since the vinyl nitrene formed by thermolysis of the oxazaphospholes is structurally very similar to the N-arylbenzimidoyl nitrene described above, it might have been expected that a similar type of rearrangement would have taken place. Nevertheless, it seems quite likely that the isolation of the 2H-azirine was possible because the

o-blocking groups prevented nitrene insertion reactions from occurring. It is noteworthy that the products arising from thermolysis of the oxazaphospholes were different from those arising from deoxygenation of the corresponding 2-aryl-1-phenylnitroethenes.[195] This point will be returned to later.

(54c) The 80% pure oxazaphosphole described above was used in the thermolysis. It was assumed that the impurities present in the oxazaphosphole were products of its thermal decomposition produced during its formation. Solution thermolysis resulted in approximately 10% extrusion of triethyl phosphate, as shown by $^{31}$P n. m. r. Chromatographic work-up gave a solid which was shown to contain 6-methyl-2-phenylindole by tlc, but the yield was less than 1% by $^{1}$H n. m. r. In addition, an oil was obtained but this was shown by $^{31}$P n. m. r. to be a mixture consisting of >90% of the major component. The oil could not be further purified by distillation. The major component was identified as the ketenimine (60) (ca 50%). The I.R. spectrum exhibits a group

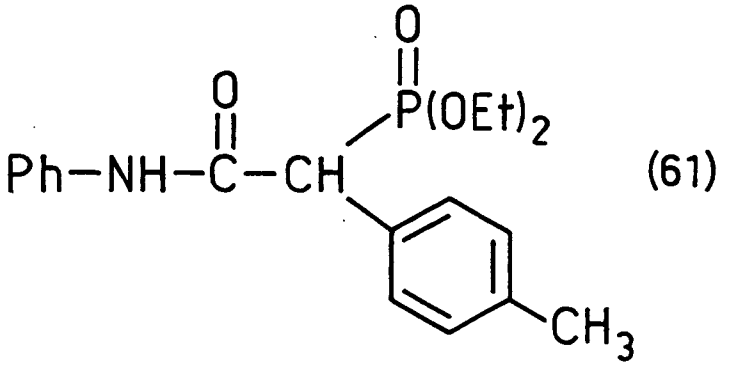



(60)

of very strong absorptions which are attributed to the major component. There are absorptions due to the P=O and P-O-C groupings, but most significantly an absorption at 2020 cm$^{-1}$ which is in exactly the right

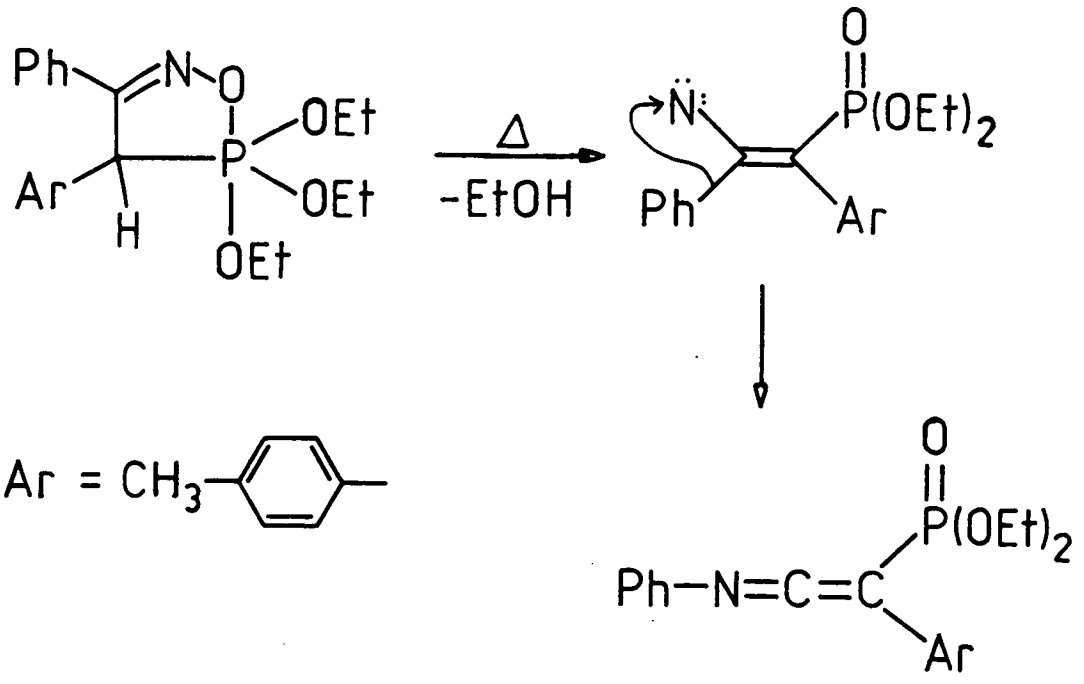
region for the C=C=N absorption of a ketenimine.[230] The $^{1}H$ n. m. r. spectrum shows the expected peaks due to two ethoxy groups attached to phosphorus and shows a singlet for the aryl methyl group. The aryl group appears as an AB quartet and the phenyl group as a singlet. The $^{13}C$ n. m. r. spectrum exhibits a phosphorus coupled doublet at 177. 9 p. p. m. which is attributed to the central carbon atom of the C=C=N group. The signal assigned to the terminal carbon occurs as a very large doublet ($J_{PC}$ = 197 Hz) at 60. 2 p. p. m. These resonances are in reasonable agreement with the published positions for ketenimines.[231] The base peak of the mass spectrum is at m/e 343 which is the parent ion of the ketenimine (60). The only significant peak at higher m/e is at 389 (10%), and this is probably due to the minor component of the mixture. The mass spectrum also has a significant peak at m/e 103 due to PhNC.

The ketenimine was found to be unexpectedly unreactive towards ethanol even in the presence of an acid catalyst, but its structure was conclusively proved by hydrolysis to the amide (61).




(61)

The formation of the ketenimine can be easily rationalised in terms of a nitrene mechanism (Scheme 99). The first step involves loss of ethanol from the oxazaphosphole to give the nitrene. Interestingly,



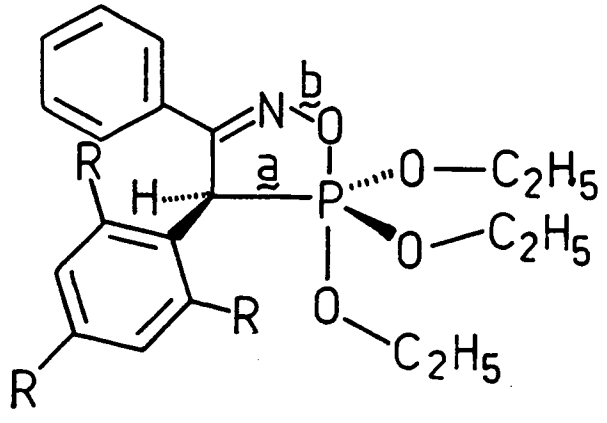

Scheme 99

the base peak in the mass spectrum of the oxazaphospholes is due to loss of ethanol from the parent ion. Subsequent phenyl migration to the electron deficient nitrogen then leads directly to the product. Once again, a concerted mechanism cannot be ruled out.

The very small amount of triethyl phosphate formed in this case would obviously result in the formation of only a very small proportion of non-phosphorus-containing products, for example the trace of indole. This result is unexpected because deoxygenation of the corresponding nitroethene gave 15% of the indole, and 12% was obtained from deoxygenation of the oxazaphosphole oxide. This therefore suggests that the formation of the indole in the nitroethene deoxygenation occurs not *via* thermolysis of the oxazaphosphole but by some other route from the oxazaphosphole oxide, perhaps *via* the nitrosoalkene with subsequent attack at the nitroso group. The same would

seem to be true of the products of deoxygenation of the o-blocked nitroethenes.

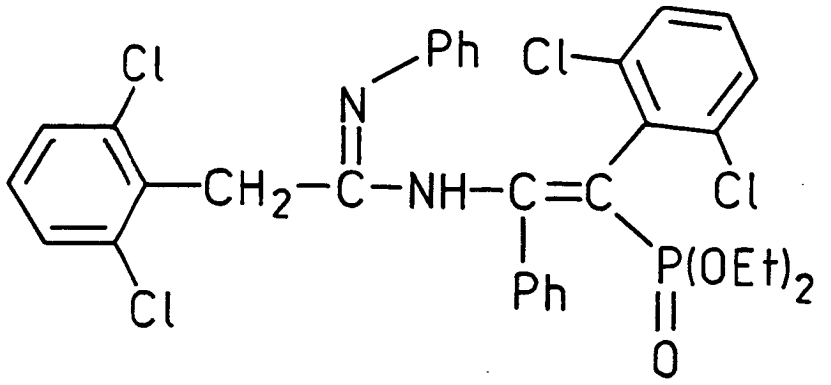
The yields of triethyl phosphate produced in these thermolyses points to an interesting steric effect in the oxazaphospholes (54). The



(54)

relative amounts of triethyl phosphate formed appear to decrease with decrease in the size of the ortho substituents. From models, it can be seen that there is significant steric interaction between the ortho substituents (where these are $CH_3$ or $OCH_3$) and the alkoxy groups on the phosphorus atom. This conclusion is supported by $^1H$ n. m. r. evidence, which shows that there is restricted rotation about the carbon-carbon bond linking the aryl ring to the heterocyclic ring. This may have the effect of lengthening the carbon-phosphorus bond a and therefore weakening it. Both bonds a and b require to be cleaved in order to extrude triethyl phosphate and such weakening of bond a would facilitate this. This therefore accounts for the increased phosphate formation on increasing the size of the ortho groups. Similarly, the formation of the phosphorylated ketenimine is explained as there is not the same driving force in this case for cleavage of the phosphorus-carbon bond.

Further evidence for nitrene intermediacy comes from the deoxygenation of (53) (Ar = 2,6-dichlorophenyl) by triethyl phosphite. In this case the reaction conditions were 15 min at 148°C. Chromatographic work-up gave two products, one of which was the 2H-azirine (6.3%). The other product was assigned as a mixture of two isomers of the amidine (62) (17%). This compound was recrystallised from

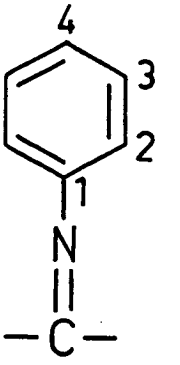


(62)

ethanol, and the spectroscopic data showed it to contain half a mole of ethanol of recrystallisation. Using a Kofler hot-stage microscope showed that the compound has two distinct melting points, presumably due to the presence of two isomers. This was confirmed by mass spectrometry, two identical mass spectra being obtained at different probe temperatures. One of the isomers predominates. The I.R. spectrum exhibits absorptions due to an NH, a C=N group, P=O, and the POC grouping. The solution I.R. also shows the ethanolic OH absorption. The $^{1}$H n.m.r. spectrum is quite consistent with the above structure. The spectrum shows the presence of half a mole of ethanol, and has the expected pattern for the ethoxyl groups attached to the phosphorus atom. The methylene group attached to the amidine functionality appears as a singlet, and the NH resonance appears to

coincide with the aromatic signals. The $^{13}C$ n.m.r. is in very good agreement with the amidine structure. A singlet at 151.5 p.p.m. is in the correct region for the amidine carbon resonance.[232] Other signals can be assigned to the phenyl group attached to the amidine nitrogen,[233] as shown in part structure (63). The carbon atoms of the

(63)

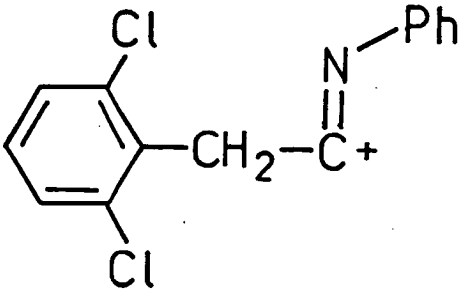



$C_1$ : 148·5 p.p.m.

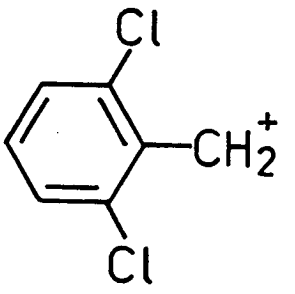
$C_2$ : 120·5 p.p.m.

$C_4$ : 121·7 p.p.m.

double bond coincide with the aromatic region and cannot be assigned unequivocably. The mass spectrum exhibits the correct parent ion (m/e 660) showing a four chlorine isotope pattern. The spectrum also shows large peaks due to the fragment ions shown below. It seems

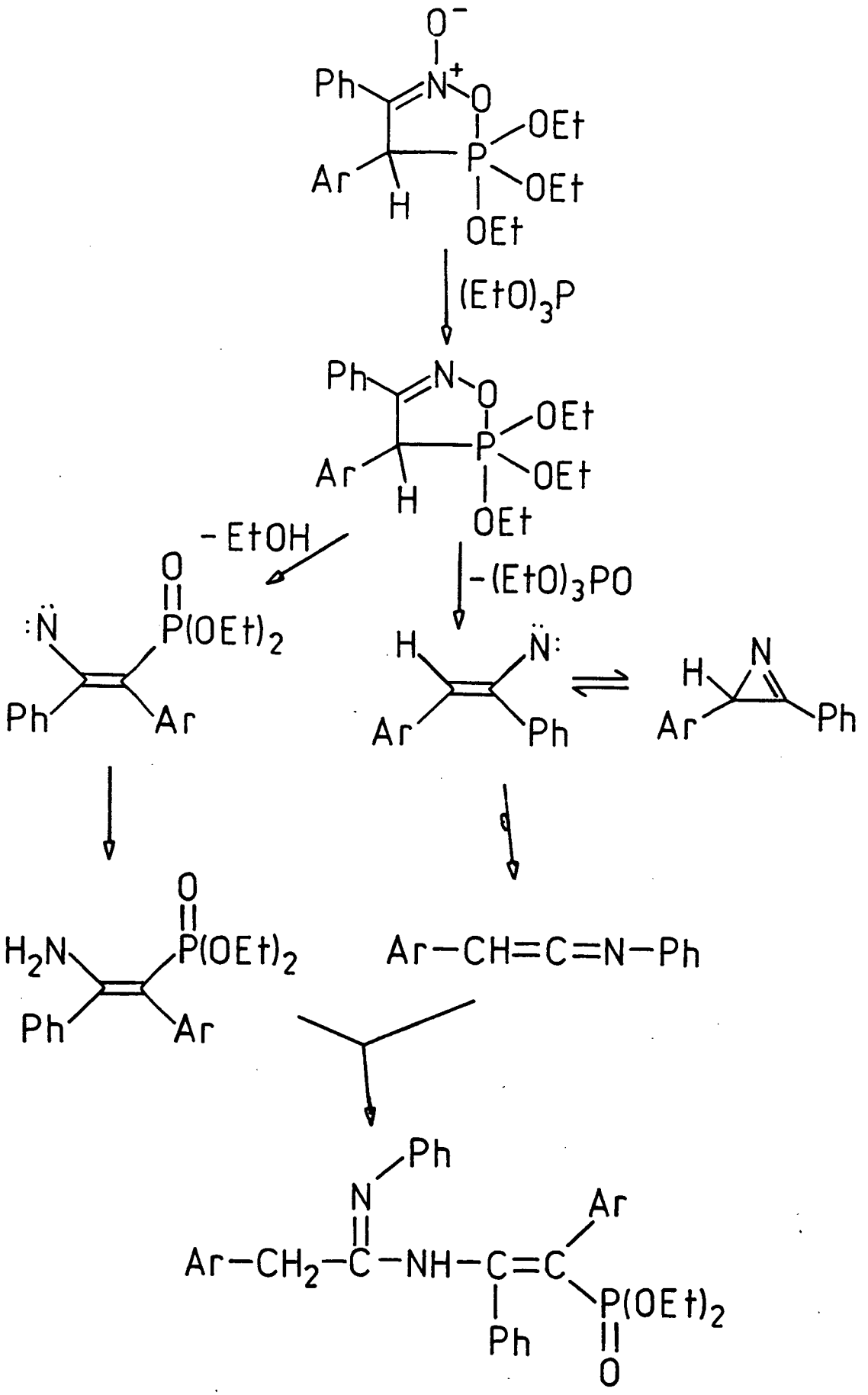



m/e 262 (54%)




m/e 159 (100%)

likely that the isomerism in compound (62) occurs at the carbon-carbon double bond since the methylene group attached to the amidine linkage appears as a singlet in the n.m.r. spectrum and is therefore not significantly affected by the change in stereochemistry.



Scheme 100

The formation of both the above products can be satisfactorily accounted for by a mechanism proceeding *via* the oxazaphosphole and involving nitrene or nitrenoid intermediates of the type already discussed (Scheme 100). One of the nitrene species undergoes a Curtius-type rearrangement to the ketenimine and the other abstracts two hydrogen atoms from the solvent to give the enamine. The final reaction of the ketenimine with the amine to give the amidine is a known type of reaction.[159]

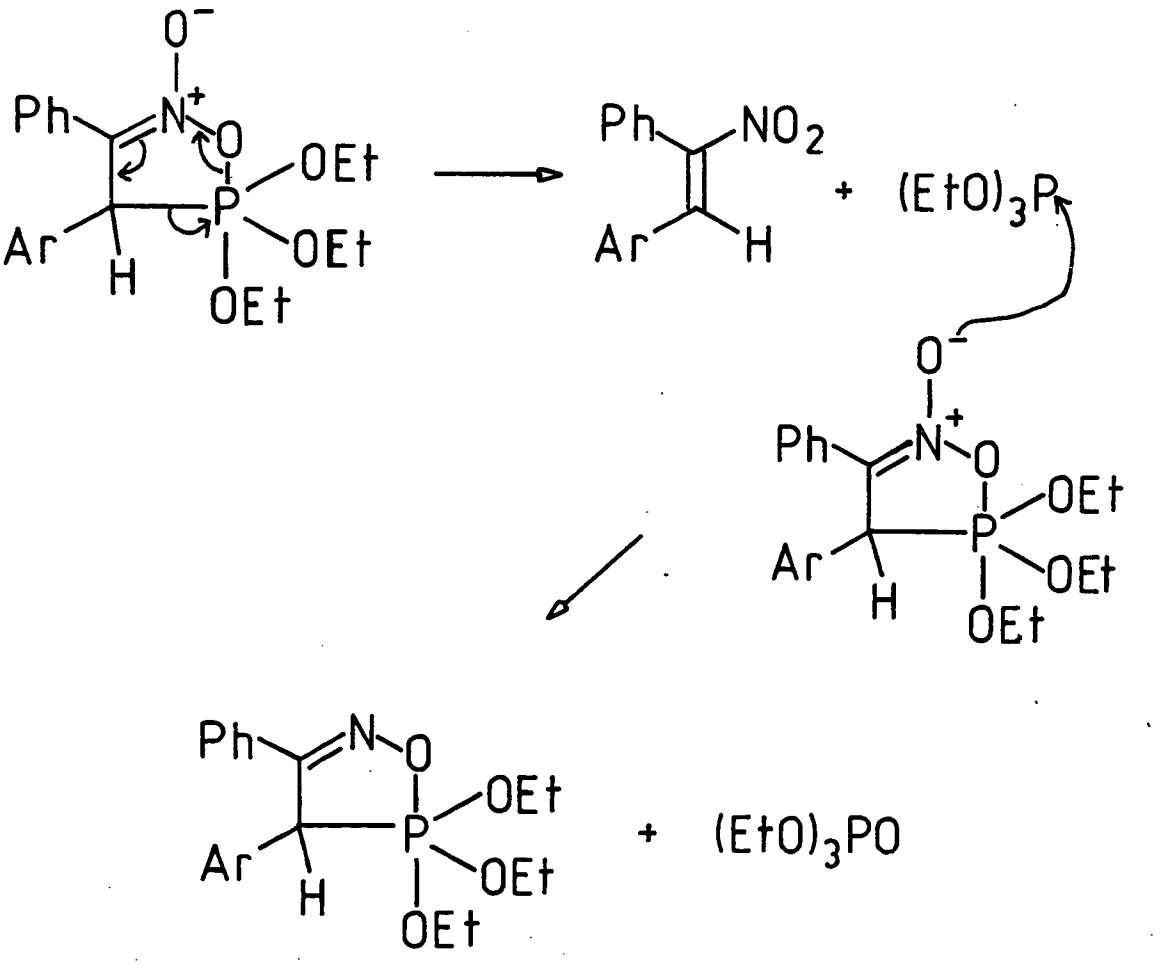
In conclusion, it has been shown that the scheme oxazaphosphole oxide -> oxazaphosphole -> nitrene -> products is certainly a feasible mechanism for the deoxygenation of 1,2-diarylnitroethenes, but it does not appear to be the only one, as evidenced by the oxazaphosphole thermolysis results. The intermediacy of the oxazaphosphole oxides does at least explain the formation of indoles from the *E*-nitroethenes without the need to invoke a double bond isomerisation because once the phosphorane is formed, the original stereochemistry of the nitroethene becomes irrelevant due to pseudorotation processes (see later). Any subsequent double bond formation from the phosphoranes could then lead to a mixture of *E*- and *Z*-isomers.

So far it has been tacitly assumed that the conversion of the oxazaphosphole oxide to the oxazaphosphole simply involves deoxygenation of the *N*-oxide function by triethyl phosphite. The reaction is, however, enormously fast by comparison with the triethyl phosphite deoxygenation of comparable *N*-oxides such as diphenylfuroxan,[24] and so it seems likely that the mechanisms are quite different. It was found that thermolysis of (53) (Ar = 2,4,6-trimethoxyphenyl) at 154°C for 30s led

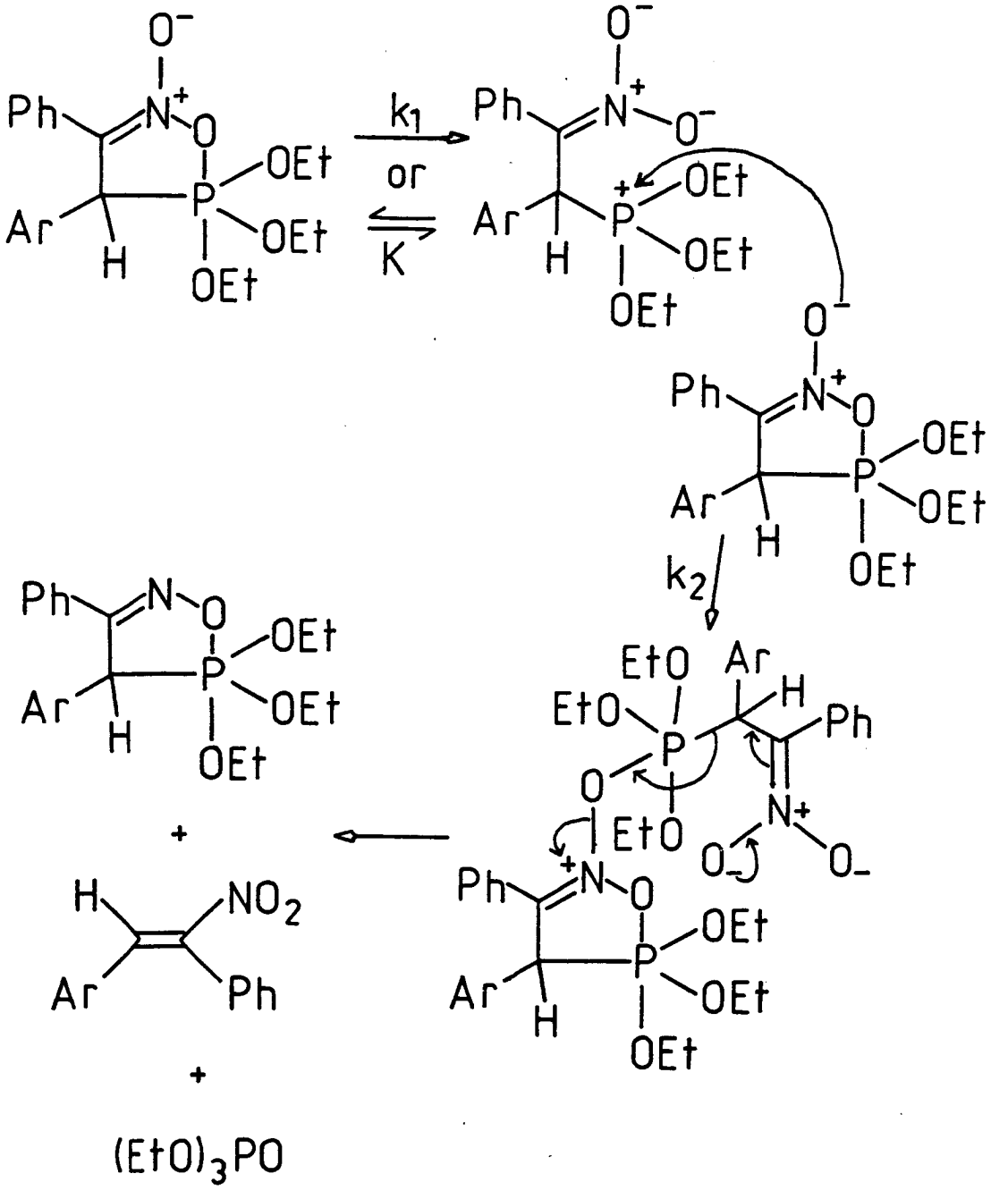
to the formation of the oxazaphosphole, triethyl phosphate, and a mixture of E- and Z-2-(2,4,6-trimethoxyphenyl)-1-phenylnitroethene (73%). This result suggests that the triethyl phosphite does not necessarily act as a deoxygenating agent, but that its true role in the conversion of the oxazaphosphole oxides to the oxazaphospholes is to convert the regenerated nitroethene back to the oxazaphosphole oxide, which then further thermolyses.

There are two possible mechanisms to account for the products of this thermolysis reaction (Scheme 101). Route A involves a retro-

Route A



Route B




Scheme 101

chelotropic reaction to regenerate the starting materials followed by deoxygenation of unchanged oxazaphosphole oxide by the triethyl phosphite. This route seems unlikely for the reasons stated above and also because no triethyl phosphite was observed by $^{31}P$ n. m. r. Route B involves ring-opening of the phosphorane to the dipolar form which then reacts

with the cyclic form to give the products *via* the intermediate shown. Ring-opening of oxazaphosphole oxides has previously been postulated by Gareev and his co-workers.[132] The ring-opening step could be either a rapid equilibrium or a slow rate determining step. If a rapid equilibrium exists, then the reaction will be second order with respect to disappearance of the oxazaphosphole oxide, and the rate constant will be $k_2K$. If the ring-opening step is the slow step, the reaction will be first order with rate constant $k_1$. The kinetics of the thermolysis were followed by $^{31}P$ n.m.r. at 76°C (349K) in $d_6$-benzene. It was found that the first order plot (ln c against t) was a straight line, apart from the first point. This rogue point is probably due to the reaction not having attained temperature equilibrium. The reaction is thus first order in oxazaphosphole oxide showing that it involves a slow ring-opening followed by rapid attack on the cyclic form. The first order rate constant was found to be

$k_{349} = (6.07 \pm 0.14) \times 10^{-4} s^{-1}$

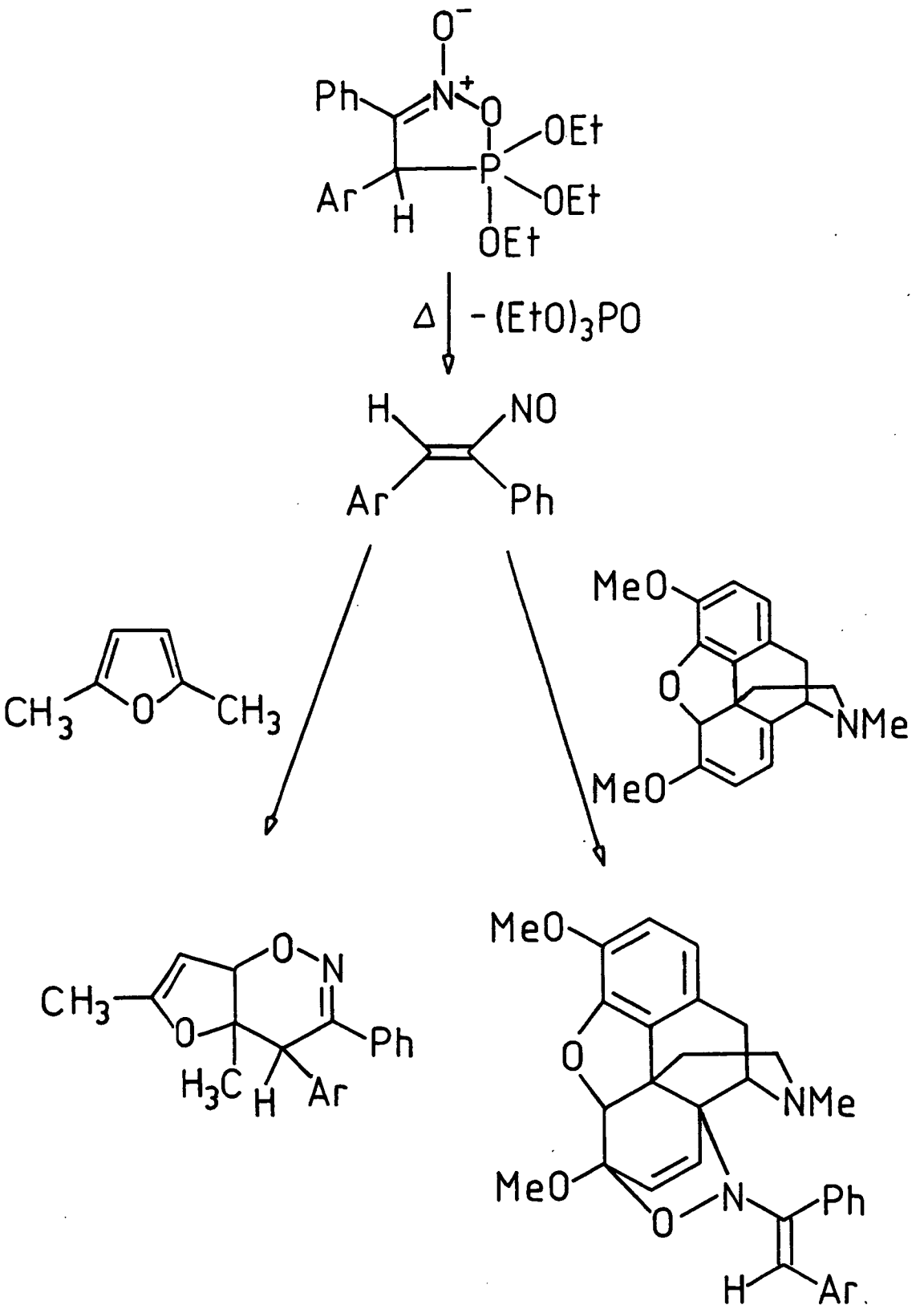
## A.4 The Question of Nitroso Intermediacy

Demonstrating the intermediacy of nitroso compounds in the deoxygenation of nitro compounds poses serious problems because of the much more facile deoxygenation of the nitroso group. In fact, there has been no really convincing experimental evidence presented in the literature to date. It was thought the present work might offer a better opportunity to detect a nitroso intermediate by attempting to trap it in the absence of any deoxygenating agent. The reasoning behind this is illustrated by Scheme 95.

The oxazaphosphole oxides are known to lose $R_3PO$ on thermolysis and it seems reasonable that in addition to the above disproportionation reaction, the nitrosoalkene might be formed. If this is the case, it should be possible to trap it and this would be good evidence of nitroso intermediacy in the deoxygenation of nitroethenes.

Nitrosobenzenes have been trapped with the alkaloid thebaine in reactions which are generally reversible.[234] Similarly, the transient nitrosocarbonyl intermediates RCONO have been trapped as crystalline adducts with thebaine and 9, 10-dimethylanthracene.[235] A number of nitrosoalkenes have been trapped as 1:1 adducts with dienes.[236] The adduct is an oxazine, formally derived by [4+2]cycloaddition of the two reactants, the nitrosoalkene acting as the four electron component. Attempts were made to trap with 2, 5-dimethylfuran and thebaine any nitrosoethene formed in the thermolysis of the oxazaphosphole oxides. The expected products are shown in Scheme 102. It can be seen that the nitrosoethene should be trapped whether it acts as a two or a four electron component. Attempted trapping of the nitrosoethene as a four electron component with 2, 5-dimethylfuran resulted in the formation of an intractable black tar. Polymerisation of the 2, 5-dimethylfuran was probably an important factor here. Trapping of the nitrosoethene as a two electron component with thebaine was also inconclusive. The solid product was found to be a mixture by tlc, and $^{31}P$ n. m. r. showed the presence of phosphorus-containing products. $^{1}H$ N. m. r. suggested that the solid was principally thebaine, and there was no convincing evidence for the presence of the adduct. The mass spectrum was similarly inconclusive.

Another way of detecting the nitrosoalkene is to try to observe an




Scheme 102

oxazaphosphole formed by reaction of the nitroso compound with a phosphorus(III) reagent. In other words, if the oxazaphosphole oxide partially decomposes via the nitrosoethene, then deoxygenation of an

oxazaphosphole oxide derived from triethyl phosphite with another tervalent phosphorus reagent should lead to a mixture of two possible oxazaphospholes. Such a reaction was attempted using dimethyl phenylphosphonite as the deoxygenating agent. The reaction produced the expected oxazaphosphole but also a compound exhibiting a peak at -16.5 p.p.m. in the $^{31}$P n.m.r. Also observed were triethyl phosphite, triethyl phosphate, and dimethyl phenylphosphonate. The peak at -16.5 p.p.m. is probably due to the oxazaphosphole derived from dimethyl phenylphosphonite. A control experiment showed that it was not formed by reaction of the phosphonite with the oxazaphosphole derived from triethyl phosphite. In addition, it cannot be totally accounted for by reaction of the phosphonite with the nitroethene produced in the disproportionation reaction because it would not be possible to obtain more oxazaphosphole than triethyl phosphate, whereas the actual ratio is ca 2:1. The crucial observation is that of triethyl phosphite, formed in the same amount as the triethyl phosphate. It was shown that there was no reaction between triethyl phosphate and dimethyl phenylphosphonite, and so the phosphite must arise by a different route. The only reasonable explanation would seem to be displacement of triethyl phosphite from the oxazaphosphole oxide by the phosphonite, although only the original oxazaphosphole oxide was observed in the $^{31}$P n.m.r. If this is indeed the case, then the formation of a phosphonite-derived oxazaphosphole can be completely accounted for, and the intermediacy of the nitrosoethene remains unproved.

An important point to demonstrate would have been that the reaction of a 1,2-diarylnitrosoethene with triethyl phosphite does in fact give an oxazaphosphole, and it would also be useful to check that such nitrosoethenes

form stable adducts with 2, 5-dimethylfuran and thebaine. Nitrosoalkenes are a relatively little known class of compounds and have been isolated in only a few cases[237] where the presence of bulky substituents at the β carbon atom lowers their reactivity. This of course would also lower their reactivity towards oxazaphosphole formation and so is somewhat self-defeating. A number of attempts were made to synthesise the previously unknown 1, 2-diphenylnitrosoethene.

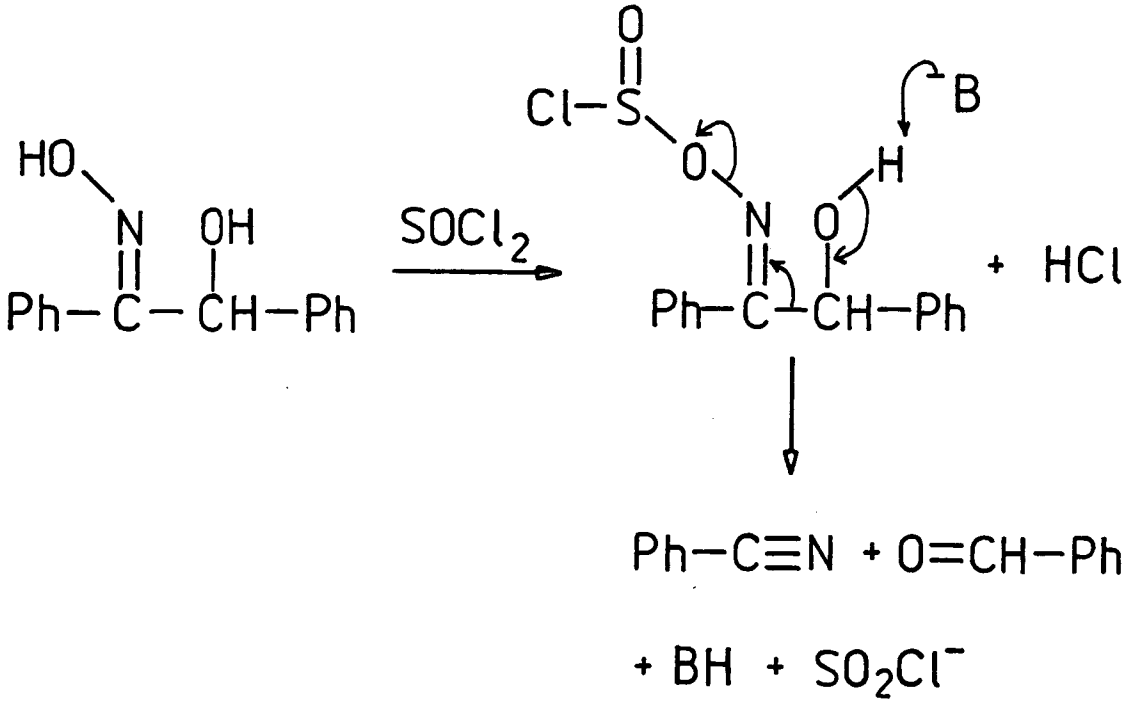
One of the routes which was envisaged was by dehydrochlorination of 1-chloro-1, 2-diphenyl-2-nitrosoethane dimer. This dimer (a nitrosochloride) is prepared by reaction of trans-stilbene with nitrosyl chloride, and could not be obtained pure in spite of the fact that its I.R. spectrum agreed with that reported for the cis and trans dimer.[238] The first attempted dehydrochlorination was by refluxing a suspension of the nitrosochloride in methanol with excess pyridine.[239] 36% of the nitrosochloride was recovered unchanged, and the other product on work-up was an intractable tar. 1, 5-Diazabicyclo[5.4.0]undec-5-ene (DBU) has been shown to be a good acceptor of hydrogen halide, and the yields of alkenes formed by the dehydrohalogenation are high.[240] It was thought that this might be more successful if the nitrosoalkene was susceptible to nucleophilic attack, because although DBU is a strong base, its nucleophilicity is low. Equimolar amounts of the nitrosochloride and DBU were reacted in DMSO at 70-80°C giving a multi-component oil (tlc) from which no identifiable products could be isolated.

In their trapping experiments with dienes, Faragher and Gilchrist[236] generated α-nitrosostyrene by the reaction of α-chloroacetophenone oxime with anhydrous sodium carbonate in dichloromethane. The same method was used to dehydrochlorinate the nitrosochloride. A large amount of

solid was recovered, and this was shown by I.R. to contain unreacted sodium carbonate, although sodium chloride may also have been present. Work-up of the solution gave a small amount of a white solid which appeared to contain a nitro group (I.R.). The mass spectrum also showed the loss of a nitro group and suggested that the compound was a nitrostilbene. It is well known that macrocyclic polyethers (crown ethers) form stable complexes with salts of alkali metals, both in solution and in the solid state.[212] This is of great utility in the solubilisation of ionic salts in organic solvents and is a most useful property of these compounds. In view of this property, it was thought it might be useful to repeat the previous experiment in the presence of a crown ether so that the salt was in solution. The reaction was carried out in dichloromethane using [18]crown-6, anhydrous potassium carbonate, and the nitrosochloride, with a little methanol added to assist solubilisation. A solid recovered after the reaction was shown to contain potassium carbonate, although there may also have been some potassium chloride present. Work-up of the solution gave a brick-red solid which on the basis of the available evidence appears to be the complex of [18]crown-6 with potassium chloride. The evidence was not conclusive, however. Chromatographic work-up gave stilbene, although its origin is not clear.

As a final attempt at dehydrochlorinating the nitrosochloride, the nitroso compound was contained in a Soxhlet thimble and N, N-dimethylaniline was used as the base, but this also proved to be unsuccessful. It seems quite likely that many of the problems encountered in the above reactions arose from the very low solubility of the nitrosochloride in common organic solvents.

Two attempts were made to prepare α-chloro-α-phenylacetophenone oxime as a precursor to 1, 2-diphenylnitrosoethene. The oxime is an isomer of the nitrosochloride used in the above reactions, and it was hoped it might be more soluble, thus alleviating some of the problems experienced previously. An attempt was made to chlorinate α-benzoin oxime by treatment with thionyl chloride under standard conditions. The product obtained was an almost colourless liquid which was shown by I. R. to be a mixture of benzaldehyde and benzonitrile. This indicates that the thionyl chloride has brought about dehydration of the molecule, accompanied by carbon-carbon bond cleavage (Scheme 103). The base, $B^-$, involved in the second step




Scheme 103

could be $Cl^-$, or $SO_2Cl^-$, or even thionyl chloride itself. This type of dehydration reaction has an analogy in the formation of a furazan from a dioxime by reaction with thionyl chloride.[241] The result of the chlorination reaction seems to indicate a preference for attack on the oxime hydroxyl

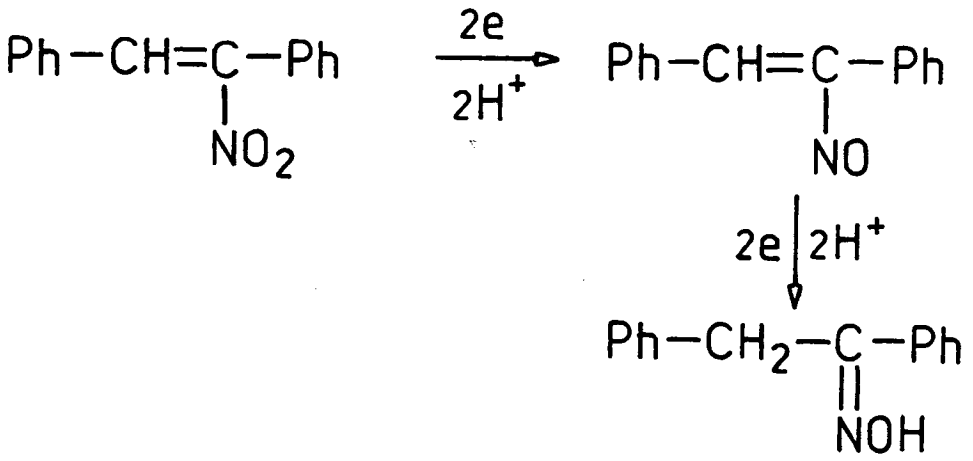
group and suggests this route to the desired product is of little use. An alternative route by oximation of desyl chloride was also a failure.

Another possible route to the nitrosoethene which was considered was the dehydration of α-benzoin oxime with acetic anhydride. In practice, the required dehydration did not occur and the product appeared to be the mono-acetoxy derivative, although the mass spectrum also showed a peak due to the di-acetoxy compound. The position of the acetyl group in the mono-acetylated derivative was not determined. Attempted thermal elimination of acetic acid was not successful.

A possible alternative to the dehydrochlorination reactions was the dehydrotosylation of the oxime of benzoin tosylate. As the tosylate ion is such a good leaving group, it might be supposed that elimination of p-toluenesulphonic acid would be easier than removal of hydrochloric acid. It was anticipated that the formation of the oxime would be the difficult step, and this did indeed prove to be the case, unreacted benzoin tosylate being recovered unchanged in 81% yield.

In general, nitroso compounds are very difficult to prepare from the corresponding nitro compounds because they themselves are usually more reactive than the nitro compound towards the reducing agent being used. It has been shown,[242] however, that nitrosoarenes can be made from the corresponding nitro compounds by electrolytic reduction in the presence of an arene sulphinic acid. The sulphinic acid is a nitroso protecting reagent and traps out the nitroso compound as a stable, non-reducible N-substituted hydroxylamine. The nitroso compound is then regenerated by basic hydrolysis. The nitroso compound is formed from the nitro compound by a two electron reduction.[243] An electrolytic reduc-

tion of 1, 2-diphenylnitroethene was attempted using benzene sulphinic acid as the protecting reagent. Initial polarographic study of the reduction gave the half-wave potential (-0.15V vs. S.C.E.) and also showed that the benzene sulphinic acid was not electroactive. A controlled potential preparative scale reduction was then carried out in 1N sulphuric acid/ ethanol (1:1) at 0°C, and a potential of -0.5V. It was found that instead of the required two electron change, a four electron reduction took place (Scheme 104[244]). Work-up[245] of the reaction mixture gave a product

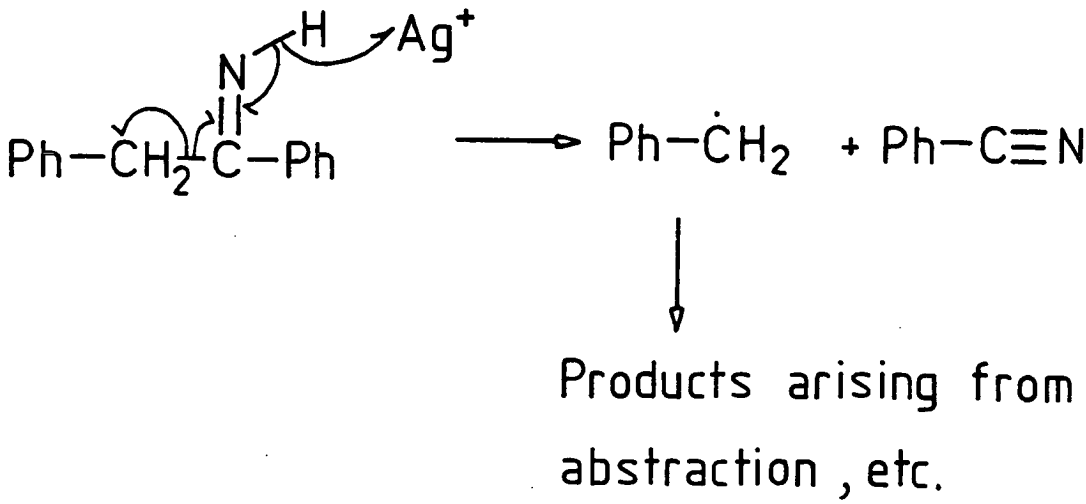



Scheme 104

which appeared to be a mixture of deoxybenzoin oxime and deoxybenzoin, probably formed by acid catalysed hydrolysis of the oxime. It appears that the nitroso compound is reduced so rapidly that it has insufficient time to diffuse away from the electrode and react with the benzene sulphinic acid, and so it is not trapped out.

A final attempt was made to synthesise 1, 2-diphenylnitrosoethene by oxidation of phenylbenzyl ketimine. Because of the likely sensitivity of the nitroso compound towards oxidation, a mild oxidising agent was required to convert the imine to the nitroso group. Such a substance is the silver carbonate on celite reagent,[185] which has been used as a mild

oxidising agent for primary and secondary alcohols. It has also been used to oxidise hydroxylamines to nitroso compounds.[246] Mild oxidation of the ketimine using this reagent gave deoxybenzoin as one of the products. This may have been produced by hydrolysis of the ketimine by water formed in the oxidation. The I.R. and mass spectrum of the residue also showed the presence of deoxybenzoin. Additionally, the I.R. exhibited an absorption at 2235 $cm^{-1}$, which is in exactly the same position as the nitrile absorption of benzonitrile. The benzonitrile is probably formed by oxidative cleavage of the imine, perhaps by a radical process involving the silver ion (Scheme 105). The benzyl radical could then possibly be oxidised to



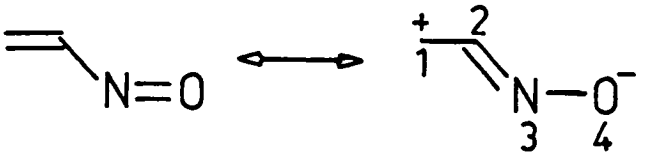

Scheme 105

benzoic acid, or it could abstract a hydrogen atom to give toluene. There was, however, no convincing evidence for the presence of either of these, although the mass spectrum did show a peak at m/e 121 which is one mass unit less than the parent ion of benzoic acid.

It is probable that the expected high reactivity of the nitrosoalkene is a major contributory factor in the failure to isolate it from any of the above reactions. Hückel molecular orbital calculations[247] (Table 7) show that the $\alpha,\beta$-unsaturated nitroso system is by far the most effective "Michael

Table 7

M. O. calculations for nitrosoalkenes[247]

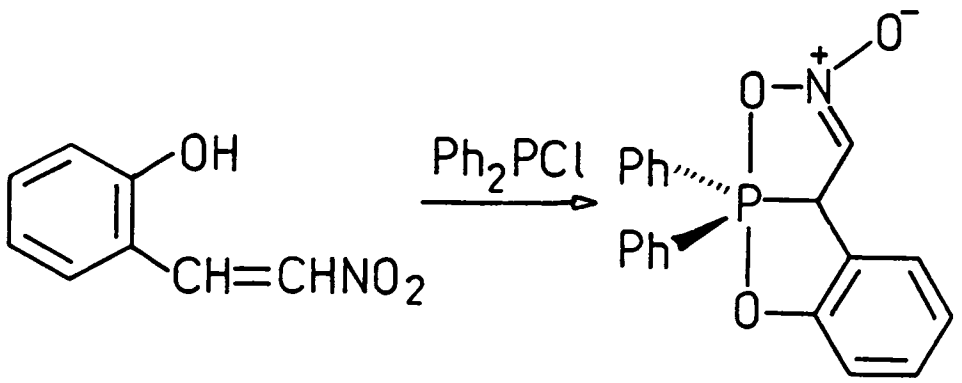


| Bond | π-Bond order | Atom | Charge density |
|---|---|---|---|
| 1-2 | 0.399 | 1 | 0.263 |
| 2-3 | 0.783 | 2 | 0.624 |
| 3-4 | 0.331 | 3 | 1.270 |
| | | 4 | 1.843 |

acceptor," as demonstrated by a 1,4-dipolar contribution very significantly above that of the α,β-unsaturated carbonyl and nitro systems. This would tend to suggest that if 1,2-diphenylnitrosoethene could be made, it would react with tervalent phosphorus reagents to give oxazaphospholes. In the absence of any tangible evidence, however, this part of the mechanistic scheme must remain in doubt.

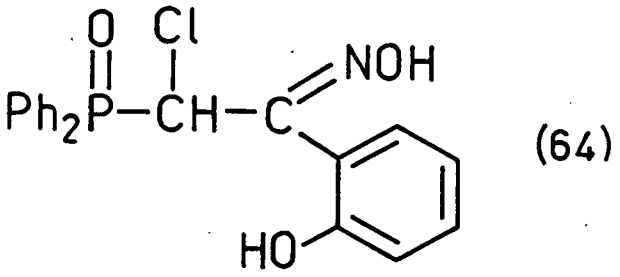
## A. 5 Miscellaneous Experiments

The reported[143] synthesis of a stable bicyclic acyloxyphosphorane prompted Dr. P. K. G. Hodgson to suggest that a similar bicyclic phosphorane of enhanced stability could be prepared by reaction of diphenylphosphinous chloride with 2-(2-hydroxyphenyl)-1-nitroethene (Scheme 106). In practice, no phosphorane was detected and reaction in benzene for five days gave a



Scheme 106

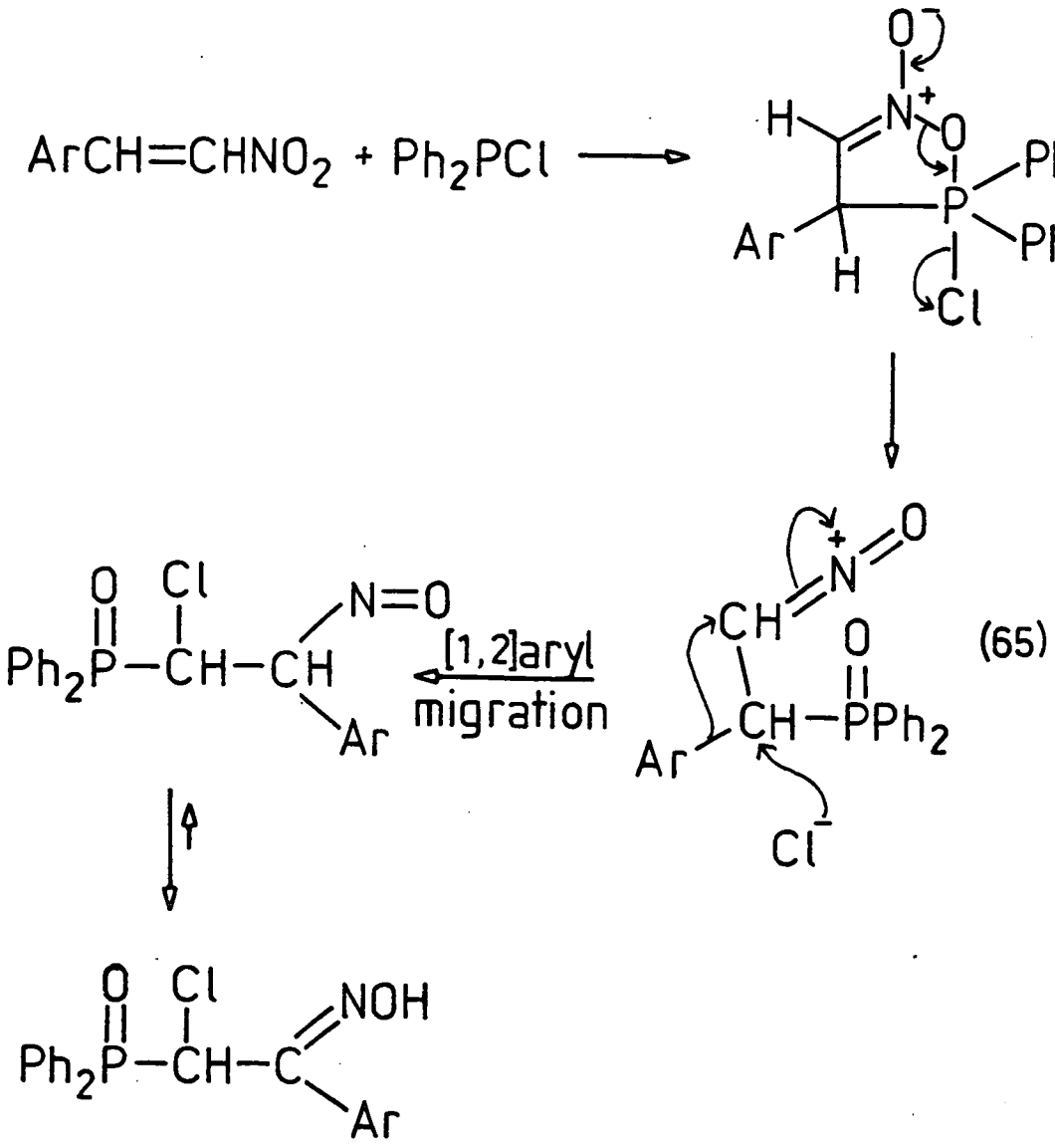
solid which has been assigned the structure (64). Key structural



(64)

information was obtained using $^{13}C$ n.m.r. spectroscopy. The evidence leading to this structural assignment will be discussed later.

There is no evidence to suggest whether (64) is formed from the bicyclic phosphorane or by attack of diphenylphosphinous chloride only on the nitroalkene system. It seems unlikely that (64) could be derived from the mechanism proposed by Gareev[128-134] for the breakdown of these phosphoranes; however, it is possible to postulate a new mechanism to explain the formation of the product (Scheme 107). A slightly modified form of this mechanism has been suggested by Teichmann et al,[141] and the $C=\overset{+}{N}=O$ function has been observed[138] in the I.R. spectrum of a postulated intermediate similar to (65) in the reaction of triethyl phosphite with ethyl $\alpha,\beta$-unsaturated $\beta$-nitrocarboxylates. The oxazaphosphole oxide is ideally set up for the internal Arbuzov reaction to give (65), which then

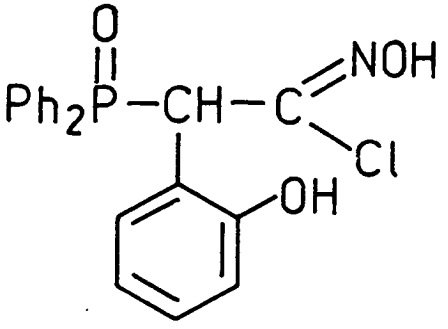



Scheme 107

undergoes attack by $Cl^-$ at the β carbon atom to give the product. The [1, 2]aryl migration is very similar to those found in the ring-opening of epoxides catalysed by boron trifluoride-etherate,[248] where the order of migratory aptitude is Ph > COOEt > Me > H[249] and $(RO)_2P(O)$ > H.[250] The preferential migration of the 2-hydroxyphenyl group is therefore reasonable, as it has the highest migratory aptitude of the three groups.

There is another possible structure (66) for the product, derived from attack of $Cl^-$ on the α carbon atom of (65), although no products similar

to (66) have been isolated in such reactions. Both (64) and (66) fit with

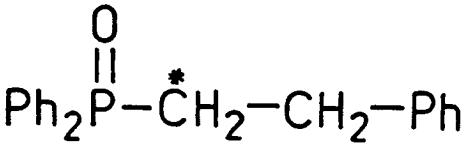


(66)

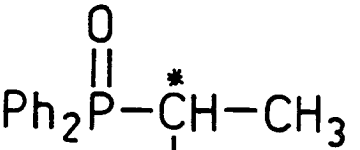
most of the analytical data obtained, but $^{13}C$ n.m.r. evidence indicates the correct structure to be (64). $^{31}P$ N.m.r. shows the presence of the P=O grouping, and the P(O).CH functionality is postulated on the basis of the $^{1}H$ n.m.r. spectrum which shows a one proton doublet with $J_{PH}$ = 10 Hz. The I.R. spectrum indicates the presence of the OH, C=N, and P=O groups, but the strong I.R. band due to the C=N grouping favours structure (64). The high stability of the compound also favours the ketoxime rather than the chloro-oxime structure. Hodgson[251] found that treatment of the compound with triethylamine and dioxan gave an immediate precipitate of triethylamine hydrochloride, but the solution showed no I.R. bands indicative of a nitrile oxide which might be expected[252] from (66). The precipitate could be a result of cyclisation involving the phenolic hydroxyl group, with consequent loss of $Cl^-$. The mass spectrum could not differentiate between the two possible structures.

Final evidence that (64) is the more likely structure comes from $^{13}C$ n.m.r. The important features of the $^{13}C$ spectrum of the compound are a doublet at 45.0 p.p.m. ($d_6$-DMSO), $J_{PC}$ = 66 Hz, and a doublet at 155.2 p.p.m., $J_{PC}$ = 6 Hz. The doublet at 45.0 p.p.m. is due to the P(O)CH carbon, and that at 155.2 p.p.m. to the C=N carbon. It is known

that in a number of cases, three-bond carbon-hydrogen coupling constants[253, 254] are significant (4-8 Hz) in both aromatic and aliphatic systems, whereas the four-bond C-H coupling constants[253] are much smaller (0-2 Hz). Considering the P(O)-CH carbon, this would show coupling to the ortho aryl proton through four bonds in the case of structure (64), and through three bonds in the case of (66); therefore, it was hoped it might prove possible to distinguish between the structures by observing long-range coupling of the resonance at 45.0 p.p.m. In the reaction product, however, no such long-range coupling could be resolved. Model compounds were prepared so that a proper comparison of long-range couplings could be made. The phosphine oxides (67) and (68) were synthesised by a Michaelis-Arbusov reaction as models for structures (64) and (66) respectively.



(67)



(68)

Unfortunately, in neither case was any significant coupling observed between the asterisked carbon and the o-protons in the phenyl ring.

Another method of using $^{13}C$ n.m.r. in structure determination is the use of chemical shifts. These are often quite constant in a series of similar compounds, and this fact was used to confirm the structure. The signal at 155.2 p.p.m., due to the C=N group, was the resonance which was studied. A series of oximes and chloro-oximes was synthesised as model compounds in an attempt to demonstrate that the position of the C=N resonance could be used to differentiate between the possible structures.

The model compounds and the positions of their C=N resonance are shown in Table 8. These results show a remarkable constancy in the chemical shift

Table 8

Chemical shifts of the C=N resonance in oximes and chloro-oximes

| Oxime | δ ($CDCl_3$) | Chloro-oxime | δ ($CDCl_3$) |
|---|---|---|---|
| $CH_3(CH_2)_3CH{=}NOH$ | 152.8 p.p.m.[255] | $CH_3(CH_2)_3C(=NOH)Cl$ | 142.6 p.p.m.[255] |
| $PhCH_2CH{=}NOH$ | 150.8 p.p.m. | $PhCH_2C(=NOH)Cl$ | 141.9 p.p.m. |
| $PhCH{=}NOH$ | 150.5 p.p.m. | $PhC(=NOH)Cl$ | 141.1 p.p.m. |
| $PhC(=NOH)-CH_3$ | 156.0 p.p.m. | | |
| Reaction product δ (C=N) : | 155.2 p.p.m. ($d_6$-DMSO) | | |
| | 155.8 p.p.m. ($CDCl_3 + CH_3OH$) | | |

of the C=N carbon within each class of compound. It is significant that the chloro-oximes exhibit a chemical shift about 10 p.p.m. lower than the corresponding oximes, and that the ketoxime, acetophenone oxime, shows a shift to low field of the aldoximes. The shift to high field of the chloro-

oximes relative to the oximes is probably due to the mesomeric electron-donating effect of the chlorine atom. In view of the consistency of the above results, and the position of the resonance in the reaction product, it seems reasonable to suggest that the product has the ketoxime structure (64) rather than the alternative chloro-oxime structure (66). It has already been noted that, in any case, this is the more likely structure on the basis of results in the literature.

It has been known[17] for some time that deoxygenation of 2-(2-furyl)-1-phenylnitroethene with triethyl phosphite gives a tar. This reaction was reinvestigated at room temperature in tert-butanol using $^{31}P$ n.m.r. The $^{31}P$ spectrum showed the appearance of two peaks in the P(V) region of the spectrum, the respective chemical shifts being close to those which typify the oxazaphospholes and oxazaphosphole oxides. At the same time, peaks due to triethyl phosphate and a compound absorbing at +15.5 p.p.m. appeared. After a longer reaction time, the peak due to the oxazaphosphole oxide (-40.8 p.p.m.) had disappeared, but there was still a significant peak due to the oxazaphosphole (-29.6 p.p.m.). The peaks at +15.5 p.p.m. and due to triethyl phosphate were large. The results suggest that although the oxazaphosphole oxide is formed, it is unstable at room temperature and spontaneously decomposes to the oxazaphosphole and triethyl phosphate. From the large amount of triethyl phosphate formed, it seems likely that the oxazaphosphole is not particularly stable either. The peak at +15.5 p.p.m. is probably due to a phosphorane decomposition product where the original phosphorus-carbon bond has remained intact. An explanation for the formation of tar in the high temperature deoxygenation can be proposed on the basis of the above results. The reaction could proceed via initial

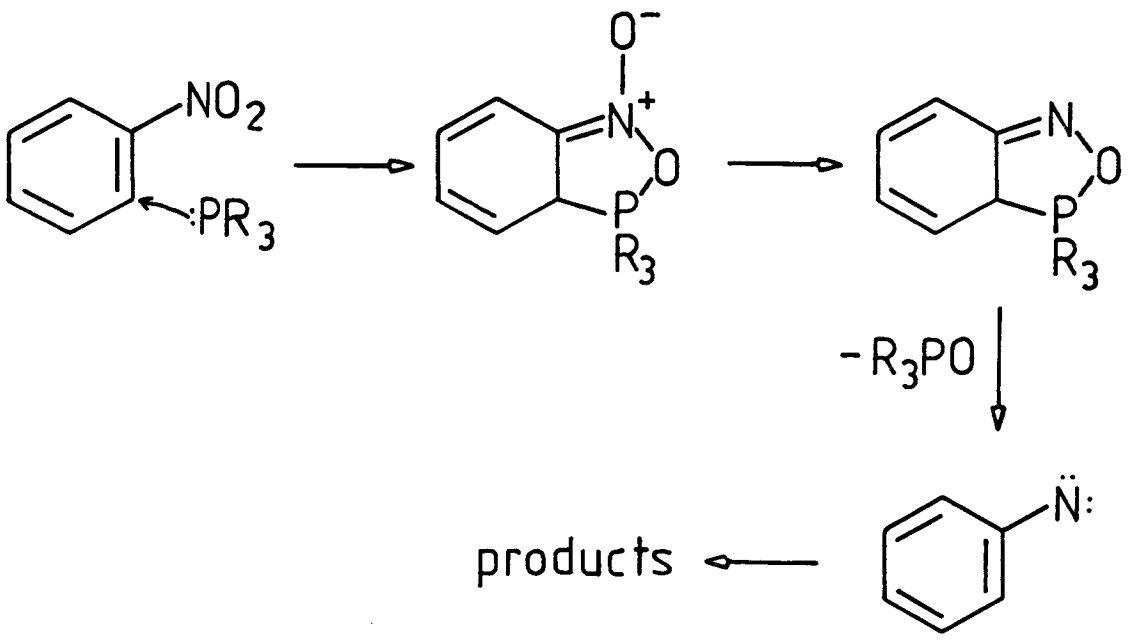
formation of the oxazaphosphole oxide which then decomposes very rapidly to the oxazaphosphole and so to the nitrene. The result would be the formation of a high concentration of nitrene and/or azirine which would probably lead to a large amount of polymerisation. The phosphoranes could also decompose to give highly polar phosphorus-containing products which would not be isolated under normal chromatographic work-up.

Cadogan and his co-workers[172] have shown that photolysis of 1, 3, 2-benzoxazaphosph(v)oles derived from dimethyl phenylphosphonite led to the formation of carbazoles by expulsion of dimethyl phenylphosphonate. A phenyl group is required on the phosphorus atom in order to provide a chromophore to absorb the light. A similar reaction was carried out with an oxazaphosphole oxide using a 15W U. V. lamp and a falling curtain reactor. The phosphorane was found to undergo cleavage with loss of dimethyl phenylphosphonate, but a complex mixture of products was obtained. Expulsion of the phosphonate should lead to initial formation of the nitroso-ethene, and the likely high reactivity of this compound could account for the large number of products. With this in mind, a photolysis was carried out in the presence of triethyl phosphite in order to deoxygenate the nitroso intermediate and so obtain nitrene-derived products. Subsequent $^{31}P$ n. m. r. showed the expected presence of triethyl phosphate and dimethyl phenylphosphonate, but no identifiable products could be isolated. Tlc showed the absence of the indole which was one of the anticipated products. It is possible in both the above photolyses that the bond between C-3 and C-4 in the oxazaphosphole ring is also being cleaved in a manner analogous to furazans,[29] resulting in the formation of complex mixtures of products.

## A.6 Conclusions

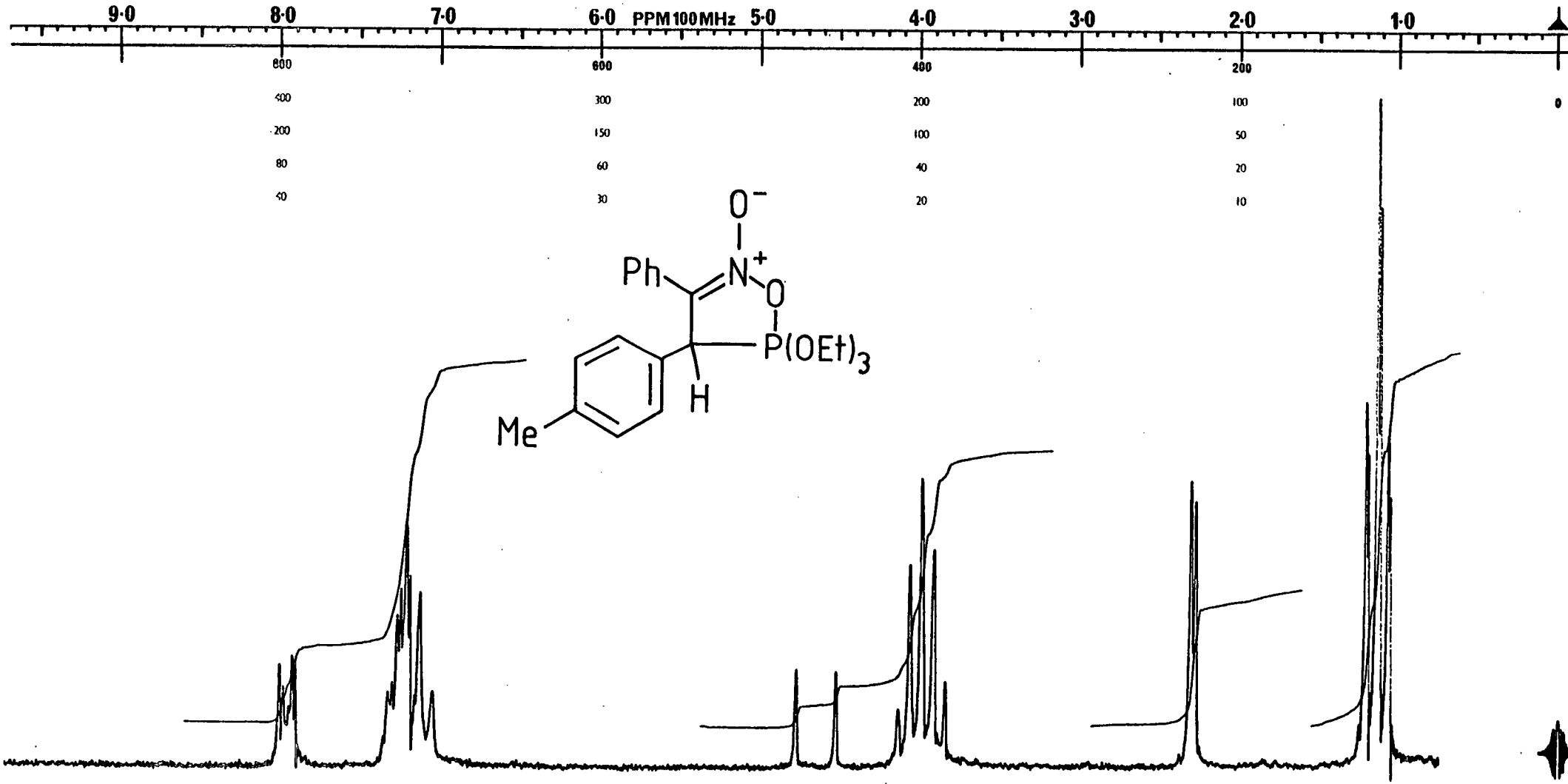
The main objective of the preceding sections was to try to prove the overall reaction scheme for the deoxygenation of 1, 2-diarylnitroethenes (Scheme 95). It has been shown that the scheme is sufficient to account for almost all the observed features of the reaction. The oxazaphosphole oxides appear to be intermediates in the route to indoles, although the results in one case suggested another mechanism might be operating simultaneously. The conversion of the oxazaphosphole oxides to the oxazaphospholes has been proved, and it has also been shown that thermolysis of these leads to the vinyl nitrene. Some of the results seemed to require a different route from the oxazaphosphole oxides, however, and the involvement of the nitrosoethene remains an attractive alternative even although it could not be demonstrated.

The reaction scheme is therefore quite reasonable as a mechanism for the deoxygenation of nitroethenes, but the possibility of a wider applicability to other nitro deoxygenations remains an unanswered question. Such a mechanism could certainly be postulated for the deoxygenation of aromatic nitro compounds (Scheme 108). It has the advantage of explaining why nitrosobenzenes are deoxygenated so much faster than nitrobenzenes because it is known that the nitroso group is a more powerful activator of an aromatic ring towards nucleophilic attack than a nitro group.[227] A major disadvantage is the loss of aromaticity involved in forming the oxazaphosphole oxide. In none of these reactions has it proved possible to detect a phosphorane intermediate[256] and so this mechanistic scheme must remain in doubt.




Scheme 108

Fig. 3 5,5,5-Triethoxy-4,5-dihydro-4-(4-methylphenyl)-2-oxo-3-phenyl-1,2,5-oxazaphosph(v)ole: $^{1}H$ n.m.r. spectrum.



## B. Spectroscopy of the 1, 2, 5-Oxazaphosph(v)ole Ring System.

### B.1 Characteristic spectroscopic features of 2-oxo-1, 2, 5-oxazaphosph(v)oles.

The cyclic phosphorane structure of the oxazaphosphole oxides is confirmed by the characteristic spectral data for these compounds. The I.R. spectra generally exhibit strong absorptions between 1550 and 1600 $cm^{-1}$, ascribed to the C=N group and the absorption due to the N-oxide function is often observed between 1200 and 1300 $cm^{-1}$.[128] Strong bands are also observed between 1000 and 1100 $cm^{-1}$ due to the POC linkage. The mass spectra are of little value, the parent ion being very weak and in some cases completely absent. Fragmentation patterns are complex and variable. The most useful technique in characterising these compounds is n.m.r. All exhibit characteristic negative chemical shifts in the $^{31}P$ n.m.r. spectrum, and there are many similarities in their $^{1}H$ n.m.r. spectra. The $^{1}H$ n.m.r. spectra of the oxazaphosphole oxides derived from dimethyl phenylphosphonite are broad at room temperature due to pseudorotation processes which will be discussed later. The spectra of those with only alkoxy groups attached to the phosphorus atom are sharp at room temperature. Fig. 3 shows an example of such a spectrum. The signals due to the ethoxy groups are split by coupling to the phosphorus. The methylene signal appears as a quintet because the proton-proton and phosphorus-proton coupling constants are identical. The spectrum shows that the ethoxy groups are all equivalent. The aryl methyl signal appears as a phosphorus coupled doublet with $J_{PH} = 3$ Hz. This represents a seven bond coupling, which is not particularly common, although a similar coupling (2.6 Hz) has been observed in the

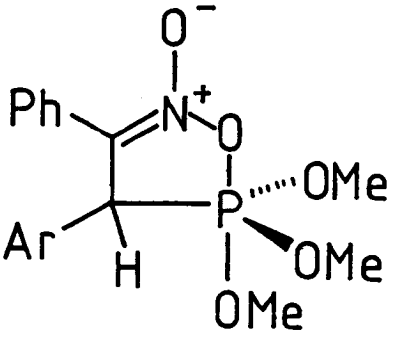
spectrum of the 4-methylbenzyltriphenylphosphonium ion.[257] The spectrum clearly shows the characteristic large one proton doublet due to the CH-P proton. Also characteristic of the oxazaphosphole oxides is the downfield two proton multiplet due to the o-protons in the phenyl ring attached to the electron-withdrawing CNO functionality.

The spectra of the corresponding oxazaphospholes, which as expected are rather similar, have been discussed in section A. 3.

B. 2 Variable temperature n. m. r. studies of 1, 2, 5-oxazaphosph(v)oles

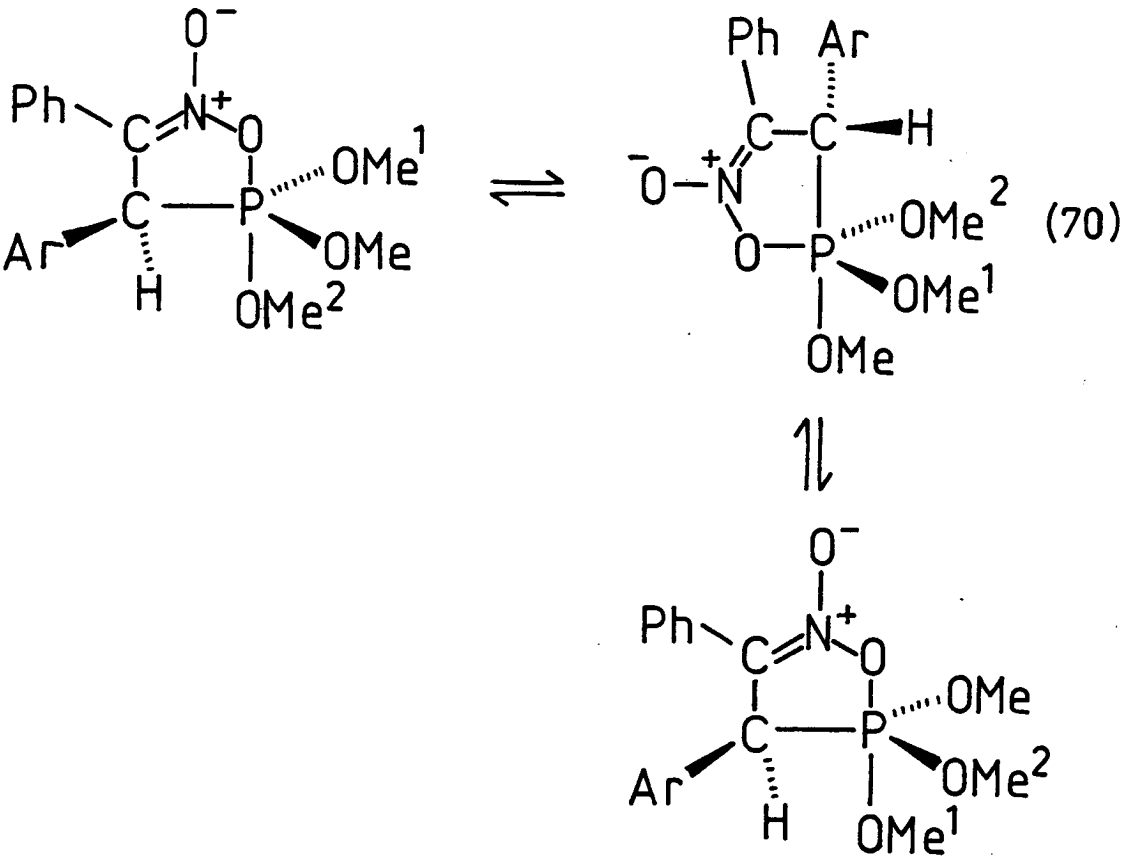
The $^{1}$H n. m. r. spectra of the oxazaphosphole oxides provide evidence for the occurrence of pseudorotation processes in these P(V) species. There are two types of pseudorotation which can operate in phosphoranes, one is Berry pseudorotation and the other turnstile rotation,[258] but in this section, only the simpler Berry pseudorotation (BPR) will be considered. Since each equatorial ligand can act as the pivot in the BPR, there are three different pseudorotations possible at each stage and consequently often a very large number of possible pathways to interconvert two isomeric trigonal bipyramids; however, only relatively few of these which are energetically most favourable need be considered.

The variable temperature (V. T.) n. m. r. spectra of the oxazaphosphole oxides (69) derived from trimethyl phosphite show the occurrence of unhindered




(69)

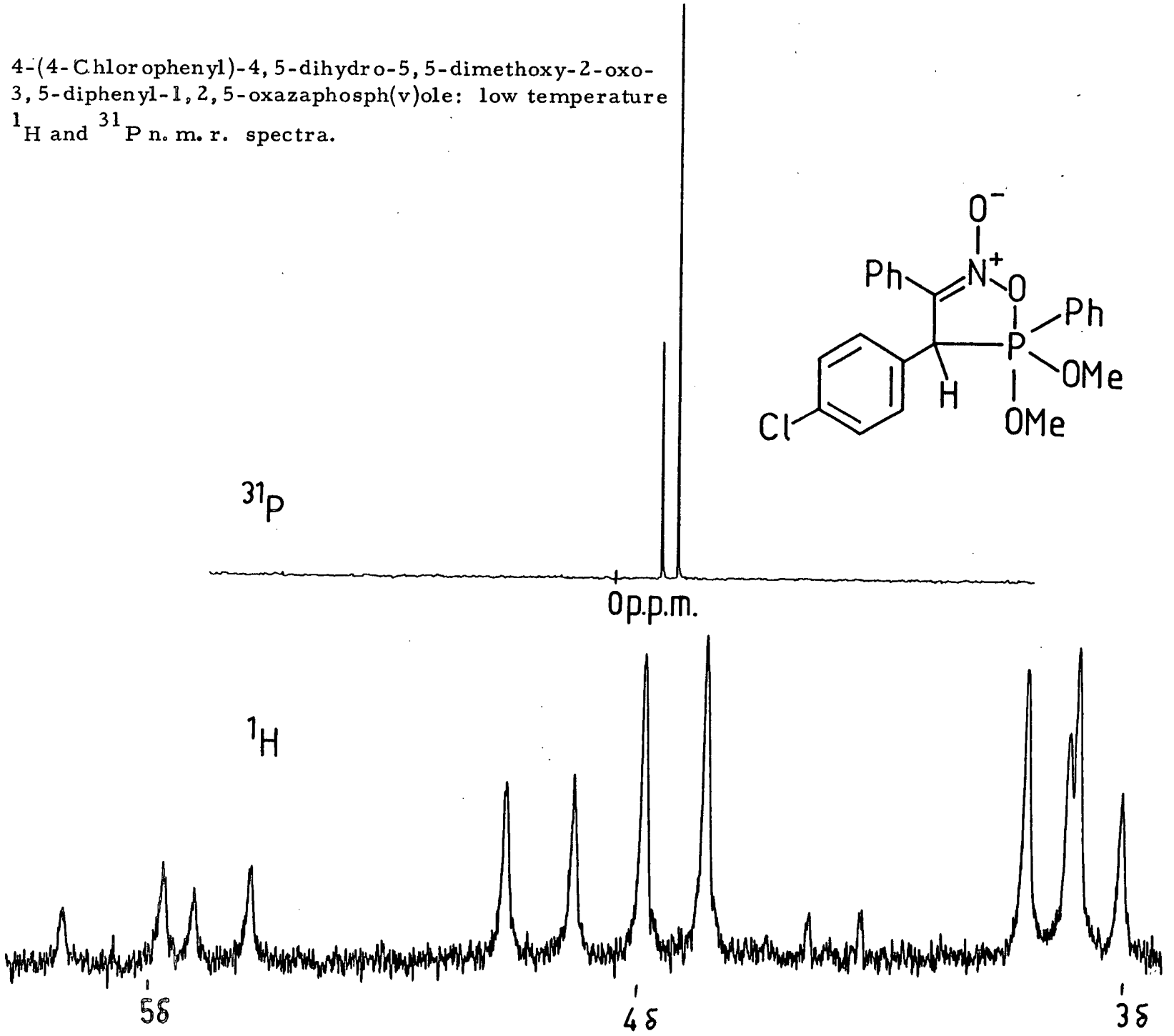
pseudorotation at room temperature as the methoxyl protons appear as a phosphorus coupled doublet. On lowering the temperature, the equivalence of the methoxyl groups is lost and at the coalescence temperature (-37 to -50°C) they appear as a broad low mound. On lowering the temperature still further, pseudorotation becomes slow on the n. m. r. time scale and the methoxyl signals appear as three distinct doublets due to the one axial and two equatorial groups. Scheme 109 shows the BPR processes required to exchange the axial and equatorial methoxyl groups. Initially, only two




Scheme 109

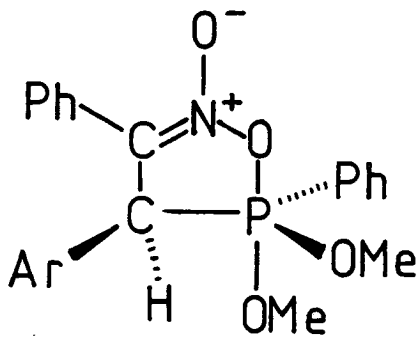
BPR's with an equatorial P-$OCH_3$ as the pivot are energetically favoured. The pseudorotation proceeds via the intermediate (70) with a carbon atom in the axial position, a situation of higher energy than either of the other two trigonal bipyramids which have more electronegative oxygen atoms occupying both axial positions. This is, however, the only significant

Fig. 4 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5-dimethoxy-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole: low temperature $^{1}H$ and $^{31}P$ n. m. r. spectra.



constraint on the pseudorotation pathway and so pseudorotation in these phosphoranes tends to be relatively easy. The free energy of activation for the above scheme was not determined as this would require a full line shape analysis.

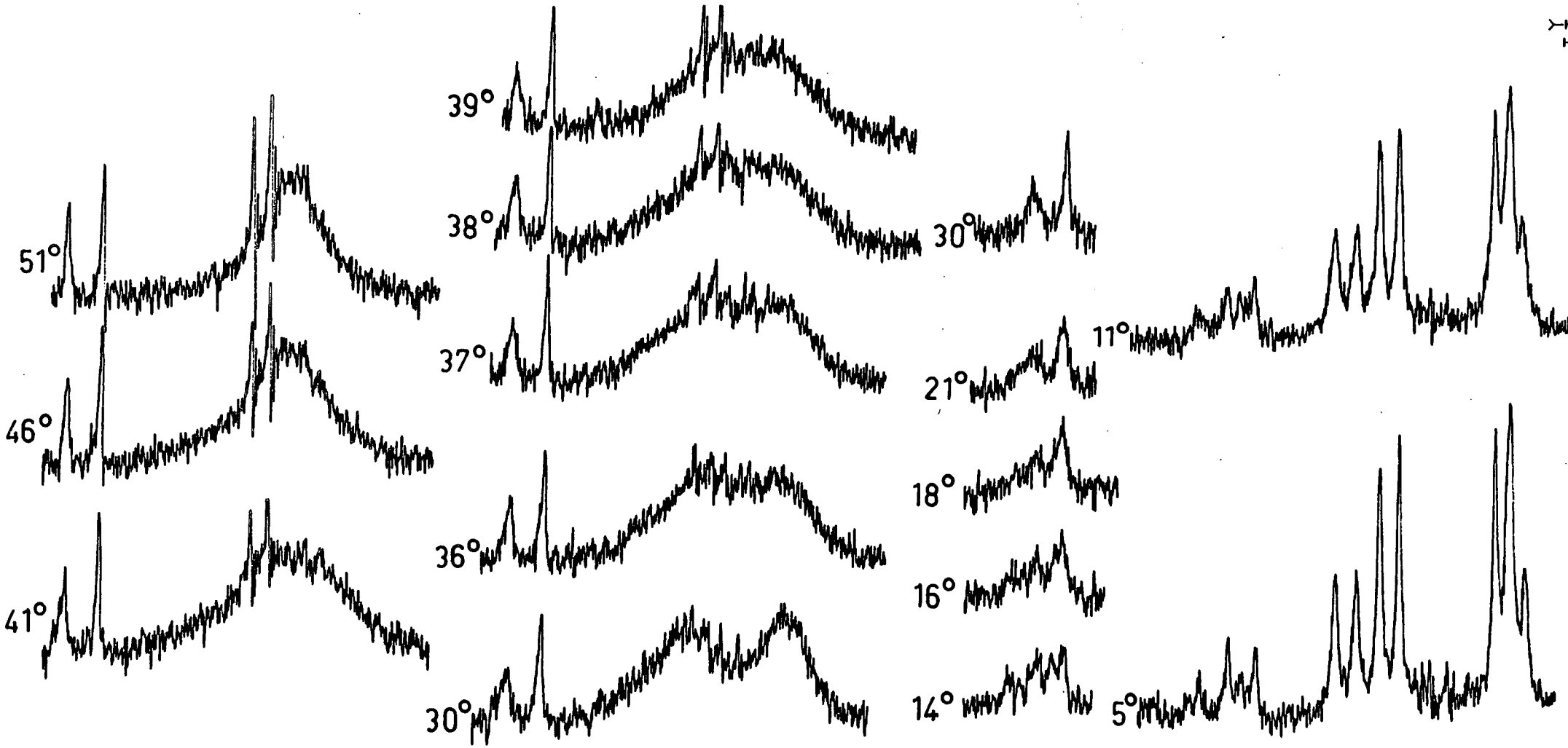
The situation is more complex when one of the methoxyls is replaced by a phenyl group (71). In addition to the chiral carbon atom, the phosphorus



(71)

atom is now also chiral and so there is the possibility of diastereoisomerism, with the 3-aryl group and the 5-phenyl group cis or trans. At low temperature, pseudorotation between the two diastereoisomers is inhibited and consequently two sets of peaks are observed in both the $^{1}H$ and $^{31}P$ n.m.r. spectra (Fig.4). The larger peaks are presumably due to the trans isomer which would be expected to be the more thermodynamically stable of the two. As the temperature is raised the $^{1}H$ n.m.r. signals due to the methoxyl groups and the proton attached to the chiral carbon atom coalesce, although the $sp^3$ proton coalescence is not particularly clear (Fig. 5). The corresponding free energy of activation for the pseudorotation process was calculated in each case using a combination of the Gutowsky-Holm equation[213] and the Eyring equation[214] (see experimental section). Although the resultant relation for $\Delta G^{*}$ strictly only applies to the exchange of equally populated sites, the use of the correct expression derived by Shanan-Atidi and Bar-Eli[259] for the free energy of activation for unequally populated

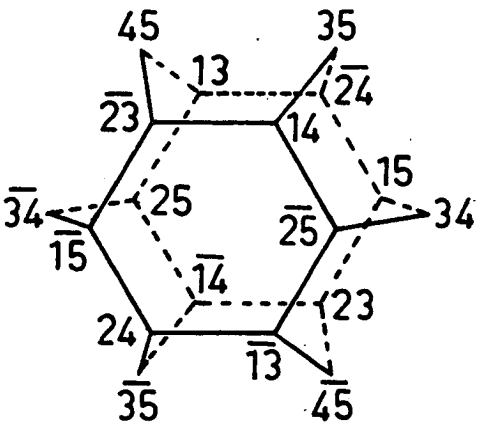
Fig. 5 4-(4-Chlorophenyl)-4, 5-dihydro-5, 5-dimethoxy-2-oxo-3, 5-diphenyl-1, 2, 5-oxazaphosph(v)ole: V. T. n. m. r. spectra of $sp^3$ proton and methoxyl resonances.



peaks gives rise to a value only ca 2 kJ $mol^{-1}$ different from the values obtained, even in the most unfavourable case. Also, the free energy difference between the values obtained for the methoxyl groups and the $sp^3$ proton are approximately constant. For this reason, the simplified equation for $\Delta G^*$ has been used throughout. The free energies of activation obtained from the coalescence of the $sp^3$ proton ranged from 62-64 kJ $mol^{-1}$, while those for the methoxyl groups were in the range 69-73 kJ $mol^{-1}$. The difference between the two values was 7-10 kJ $mol^{-1}$, a figure which cannot be explained in terms of experimental error and is therefore a genuinely significant quantity.

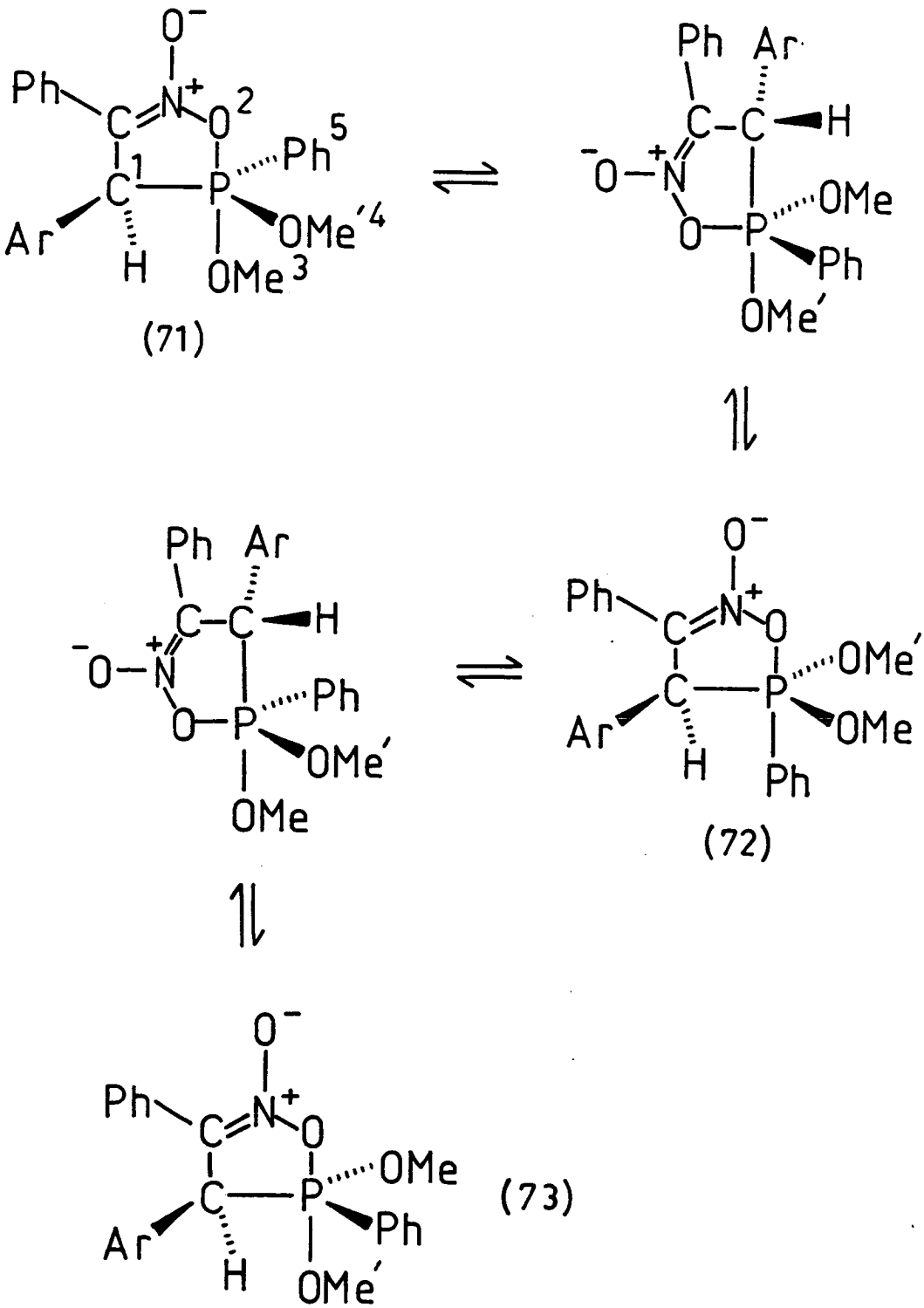
These observations can be explained in terms of the pseudorotation processes taking place. The various pseudorotation pathways were predicted using the hexa-asterane graph (Fig. 6) devised by Mislow.[260]

Fig. 6




In this graph, the pair of numbers represents the two apical ligands, while the presence or lack of a bar depends on whether the numerical order of the equatorial ligands is anticlockwise or clockwise. The twelve vertices on the front and back hexagons represent isomers with the five-membered ring axial-equatorial, whereas the six points of the star correspond to isomers with the ring equatorial-equatorial.

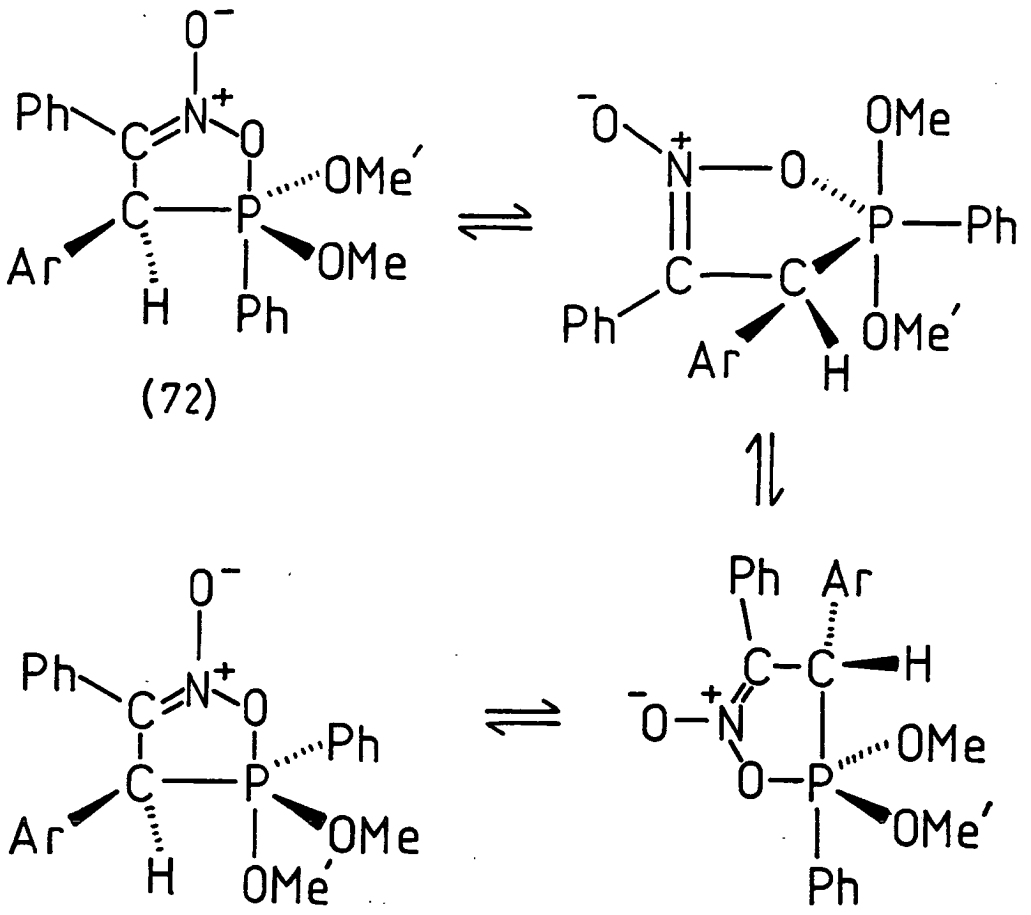
If isomer (71) is arbitrarily numbered as shown, the predicted pseudo-rotation pathways are represented by Schemes 110 and 111. Scheme 110 represents




Scheme 110

the processes required to equilibrate the diastereoisomers (71) and (73) and is

therefore responsible for the coalescence of the signals due to the proton attached



(72)

Scheme 111

to the chiral carbon atom. This corresponds to the sequence $\overline{23}$ -> 14 -> $\overline{25}$ -> $\overline{13}$ -> 24 on the hexa-asterane graph, a route involving trigonal bipyramidal intermediates with only one carbon atom in an apical position. The shorter route $\overline{23}$ -> $\overline{15}$ -> 24 involves an intermediate with two carbon atoms in apical positions and so will be less energetically favourable than the longer route shown in Scheme 110. Complete equilibration of the methoxyl groups requires a sequence linking $\overline{23}$ to $\overline{24}$, and the graph clearly shows that this is impossible without proceeding <u>via</u> one of the six trigonal bipyramidal intermediates with the five-membered ring diequatorial, a situation of high energy due to the considerable ring strain imposed by the 120°

angle at phosphorus. It can also be seen that four of these intermediates have the additional constraint of an apical phenyl ring. For this reason, it seems reasonable to assume that the pseudorotation proceeds *via* one of the intermediates 34 or $\overline{34}$, even although both these routes involve an intermediate (15 or $\overline{15}$) with two apical carbon atoms. Scheme 111 represents the sequence $\overline{25}$ -> 34 -> 15 -> $\overline{24}$. Clearly, total equilibration of the methoxyl signals requires a greater free energy of activation than equilibration of the $sp^3$ proton signals.

The relationship between the pseudorotation pathways shown above and the observed $^1H$ n. m. r. spectra is discussed below, and points out a further complicating factor which has so far not been considered. Fig. 7 shows three idealised spectra of the methoxyl resonances. (A) represents the

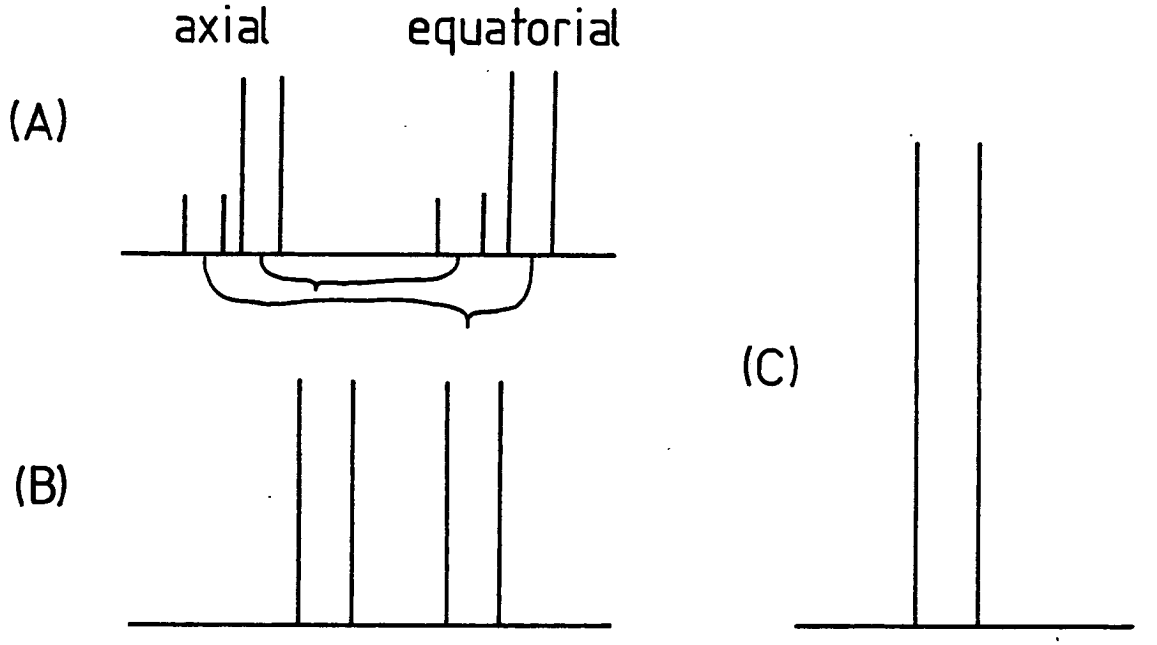
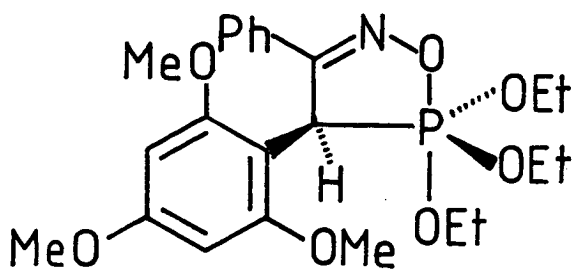



Fig. 7

situation at low temperature where the two isomers are "frozen out." The ratio of major to minor is *ca* 3:1. At the temperature represented by (B), there is equilibration between (71) and (73): the minor axial signal equilibrates

with the major equatorial and the minor equatorial with the major axial so that a "weighted" average position is obtained. At the temperature represented by (C), there is complete equilibration of the methoxyl signals and only one phosphorus coupled doublet is observed. There are therefore two coalescence temperatures for the methoxyl groups, but if the isomers are present in similar proportions, it may not be possible to distinguish case (B) clearly, and so the nature of the observed coalescence may not be obvious. In the case of the oxazaphospholes under study, the methoxyl coalescence is not clearly assignable to the $A \rightleftharpoons B$ or the $A \rightleftharpoons C$ equilibrium (see Fig. 5); however, the coalescence of the $sp^3$ proton is due to the (71) $\rightleftharpoons$ (73) equilibrium, i.e. $A \rightleftharpoons B$, and is therefore a better indication of the free energy change involved in this process. As the value obtained from the methoxyl coalescence is somewhat higher than this, it obviously sets a lower limit for the free energy of activation of the $A \rightleftharpoons C$ equilibrium. In accordance with the values for $\Delta G^*$ found here, it has previously been reported that the free energy of activation associated with placing an alkyl or aryl substituent in the apical position varies from 42-71 kJ $mol^{-1}$, whereas the free energy of activation for forming a diequatorial ring intermediate is about 84 kJ $mol^{-1}$. [261]

It has previously been shown that the m-aryl protons and the o-methoxyl protons in oxazaphosphole (54a) are non-equivalent at room temperature due

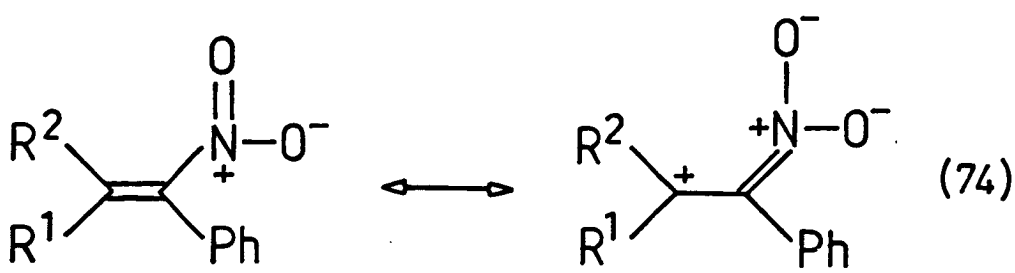



(54a)

to restricted rotation about the carbon-carbon bond joining the aryl ring to the oxazaphosphole ring. As the temperature was increased, the $^{1}H$ n. m. r. signals due to both sets of protons coalesced and then began to peak again. Two values were calculated for the free energy of activation of the rotation using the expression used above, which in this case is valid as both peaks are of equal intensity. As would be expected, both coalescences gave, within experimental error, the same value for $\Delta G^{*}$, which was 68 kJ $mol^{-1}$.

C. Steric Effects in Reactions of Nitroethenes with Tervalent Phosphorus Reagents.

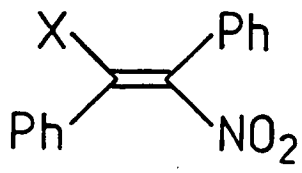
North[195] found that the high temperature deoxygenation of 1, 2, 2-triphenylnitroethene with triethyl phosphite gave a high yield (70%) of 2, 3-diphenylindole, and also detected no oxazaphosphole oxide in the low temperature reaction. The suggestion was that the presence of the additional phenyl group hindered Michael addition of the phosphite to the β-position of the double bond both by steric hindrance and by preventing coplanarity of the nitro group and the double bond, thus significantly reducing the contribution from canonical form (74). As a result, the




(74)

phosphite attacked predominantly at the nitro group leading to formation of the nitrene and consequently a high yield of the nitrene-derived product.

In the present work, it was considered it might be useful to investigate the effect of groups intermediate in size between a hydrogen atom and a phenyl ring to see if the expected trends were in fact observed. For this investigation, the nitroethenes (75) were prepared by addition of acetyl




(75) (a) X = Me (b) X = Et

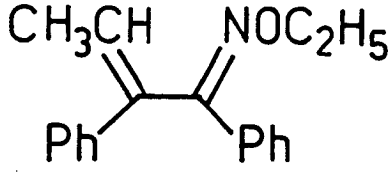
nitrate across the double bond of the corresponding α-alkylstilbene, followed by removal of acetic acid with base. The U. V. envelopes of the nitroethenes suggested their configuration was Z- (trans-) as both showed absorption maxima below 250 nm. It should be borne in mind, however, that the validity of this argument rests on the assumption that the E-isomer much more closely approaches planarity for the whole molecule than does the Z-isomer, and consequently absorbs at a much higher wavelength than 250 nm.[194] If the steric interaction between substituent X and the nitro group in the E-isomer disturbs the planarity of the molecule as much (or nearly so) as the phenyl ring/nitro group interaction, then this argument will be invalid, although there is no real reason to believe this is the case.

Formation of the oxazaphosphole oxides from reaction of the nitroethenes with triethyl phosphite in tert-butanol was investigated by $^{31}P$ n. m. r. In the case of (75a), the phosphorane formed very slowly and unreacted nitroethene remained even after 184 h. A significant amount of triethyl phosphate was also formed, perhaps via decomposition of the oxazaphosphole oxide.

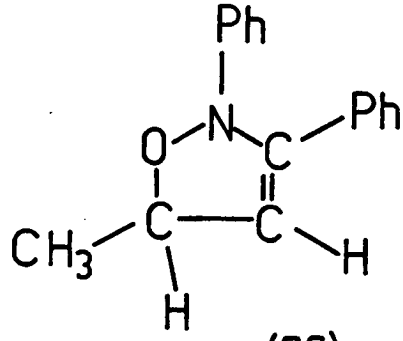
The same general trends were observed for (75b), but the amount of phosphorane formed in this case was much smaller. These observations tie in with the hypothesis that the bulkier the group on the β carbon atom, the more hindered is Michael addition and therefore phosphorane formation. The greater inhibition of phosphorane formation in the case of X=Et is almost certainly due entirely to greater steric hindrance towards the incoming phosphite . The degree of inhibition of coplanarity of the nitro group and the double bond should be effectively the same in both cases since it is the phenyl group which is on the same side of the molecule as the nitro group.

It would be expected then that the high temperature deoxygenation reaction would lead to moderate to high yields of nitrene-derived products such as indoles, and/or a dihydropyrrole in the case of (75b). In practice, this did not occur, however, and in both cases, a seemingly unique phosphite-induced rearrangement occurred without deoxygenation of the nitro group. The nature of this rearrangement will be discussed later.

In the case of (75b), the minor products (76) (4.1%) and (77) (5.4%)

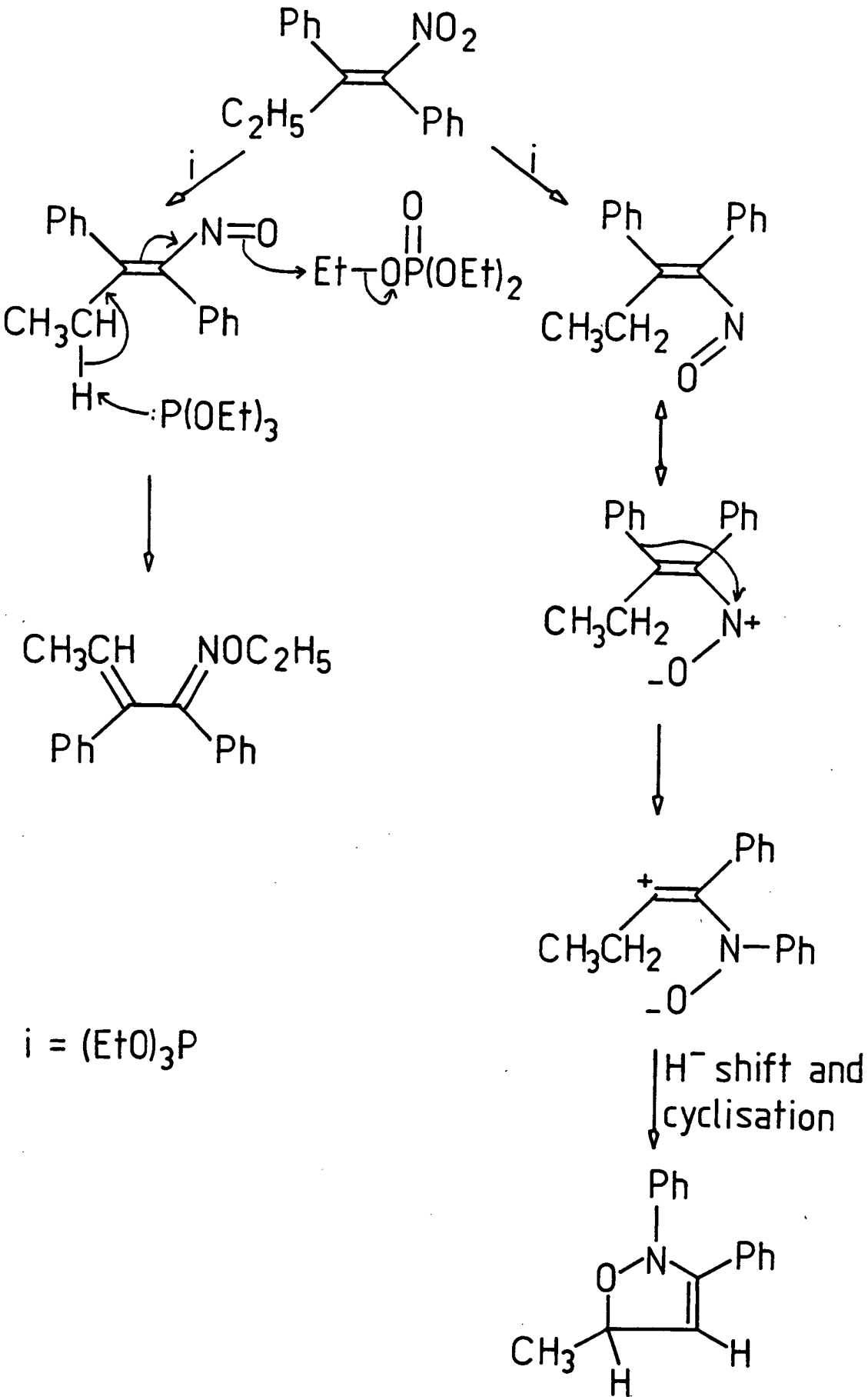



(76)




(77)

were also obtained. Both the O-ethyl oxime (76) and the isoxazoline (77) can be considered to arise via the nitroso compound (Scheme 112). (76) is formed by attack of phosphite acting as a base with concomitant ethylation


Ph
NO2
C2H5
Ph
i
i
Ph
N=O
O
Et–OP(OEt)2
CH3CH
Ph
H
:P(OEt)3
Ph
Ph
CH3CH2
N
O
CH3CH
NOC2H5
Ph
Ph
Ph
Ph
CH3CH2
N+
-O
Ph
+
CH3CH2
N–Ph
-O
i = (EtO)3P
H⁻ shift and
cyclisation
Ph
O
N
Ph
CH3
H
H

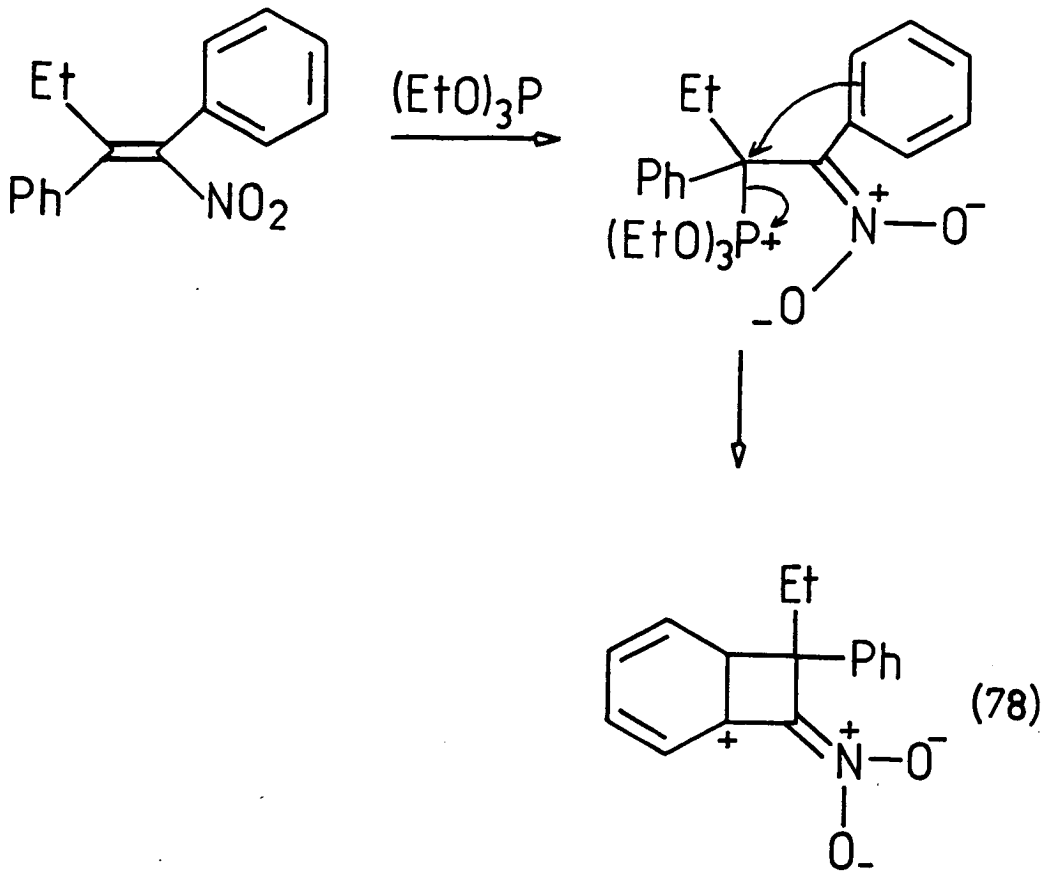
Scheme 112

by triethyl phosphate. The structure of the isoxazoline is less convincing, but a highly speculative mechanism involving phenyl migration to the nitrogen of the nitroso group followed by a [1, 2]hydride shift and cyclisation could lead to the product. The deoxygenation step would seem to require a double bond isomerisation in this case. No such minor products were isolated in the case of (75a).

As indicated above, in both cases, the main product (ca 50%) is a result of a rearrangement of the nitroethene, apparently induced by triethyl phosphite. Unfortunately, the precise structure of these products has not been ascertained. The spectroscopic data for the product arising from (75b) will be discussed along with any structural conclusions which can be drawn. Similar data was obtained for the product from (75a). The elemental analysis clearly shows that the product has the same molecular formula as the nitro compound, and the parent ion of the mass spectrum confirms this. The I.R. spectrum shows a very broad band at 2500-3300 $cm^{-1}$, indicative of a chelated OH. This is confirmed by the existence of a very sharp singlet at 11.53$\delta$ in the $^{1}H$ n.m.r. The spectrum also exhibits some quite unusual features. The methyl signal appears at very high field (0.44$\delta$) and two of the aromatic protons absorb at very low field indeed (8.2-8.4$\delta$). The methylene group is prochiral, and the integral shows that an insertion has occurred into one of the phenyl rings. It seems likely that the ethyl group is attached to an $sp^{3}$ carbon and that the stereochemistry is such that the methyl group is held over a phenyl ring or some similarly anisotropic group. The latter could also be the cause of the downfield aromatic signals. The $^{13}C$ n.m.r. exhibits five quaternaries, confirming that an insertion has occurred. There are quaternaries at 176.7, 153.5, and 97.6 p.p.m.,

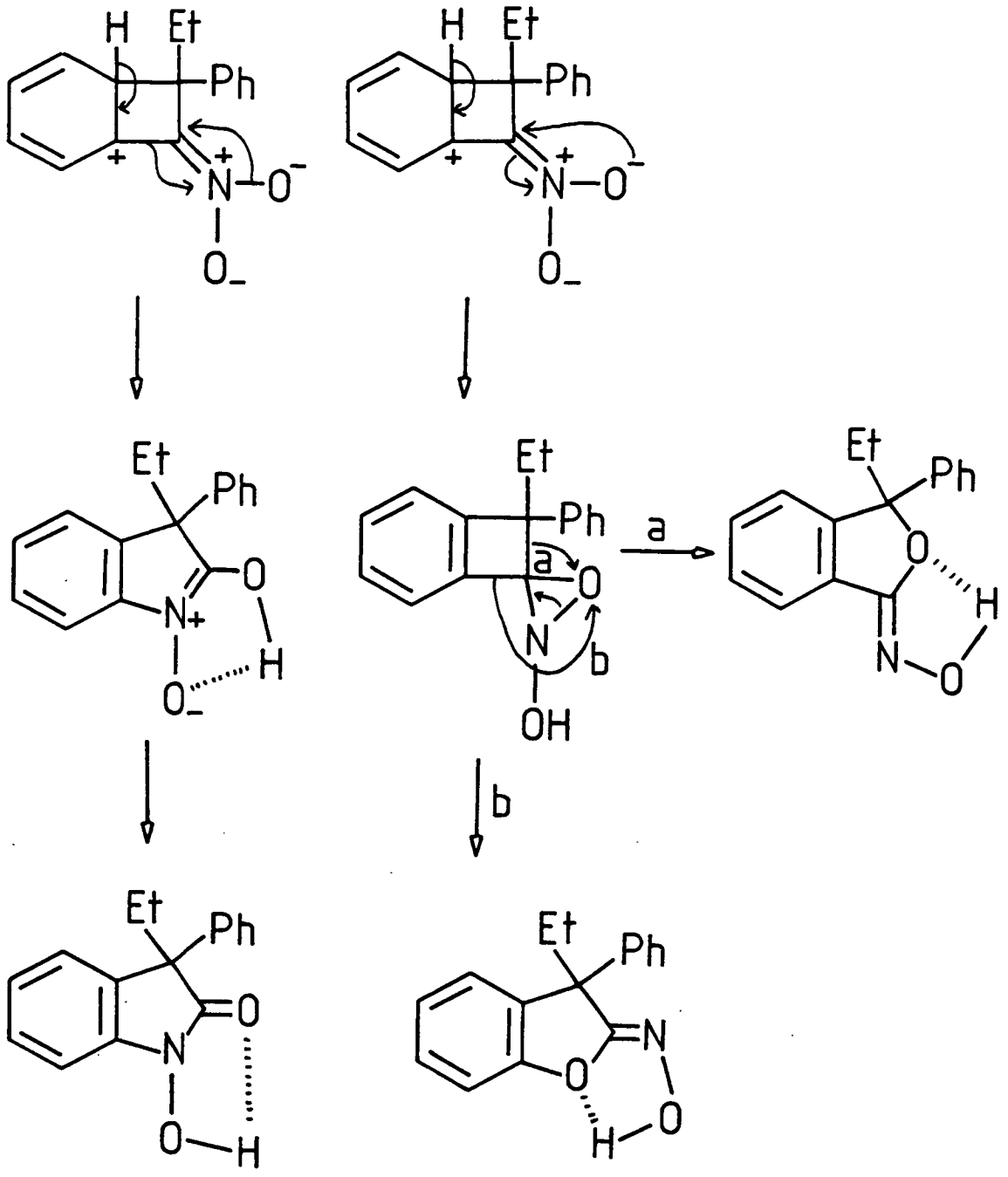
the latter of which is probably due to the ring $sp^3$ carbon. The absorption at 176.7 p.p.m. could be due to a C=O or C=N, although it is at rather low field for a C=N, and the I.R. shows no peak in the carbonyl region. The peak at 153.5 p.p.m. is probably due to an aryl carbon attached to nitrogen or oxygen, although it could also be due to a C=N group. On standing in DMSO, the compound isomerised completely to another compound which showed very similar n.m.r. spectral features, except that the OH signal was now at 4.6 δ in $CDCl_3$. The mass spectrum of the original product showed loss of 17, 29 ($C_2H_5$) and 47 mass units, with the base peak at m/e 105 (PhCO). Assuming the product does not lose an oxygen atom in DMSO, then the isomerised product appears to be an N-oxide as it shows a very weak parent ion and a strong peak at M-16.

The unidentified product was not formed by heating the nitroethene in t-butylbenzene, with or without added triethyl phosphite, or in pyridine. It would therefore appear that the reaction is not a general base catalysed reaction nor simply a thermal rearrangement, but a rearrangement induced by a large concentration of triethyl phosphite. It is reasonable to assume that the reaction involves attack of phosphite at the β-position of the double bond with subsequent formation of the intermediate (78) (Scheme 113). Several possible routes from this intermediate were considered and these are shown along with the expected products in Scheme 114. None of these products appear to fit with the observed spectroscopic data, however, and this was confirmed by comparison of the data for 3-ethyl-3-phenylphthalide and hydroxamic acid with that obtained for the unknown.




Scheme 113

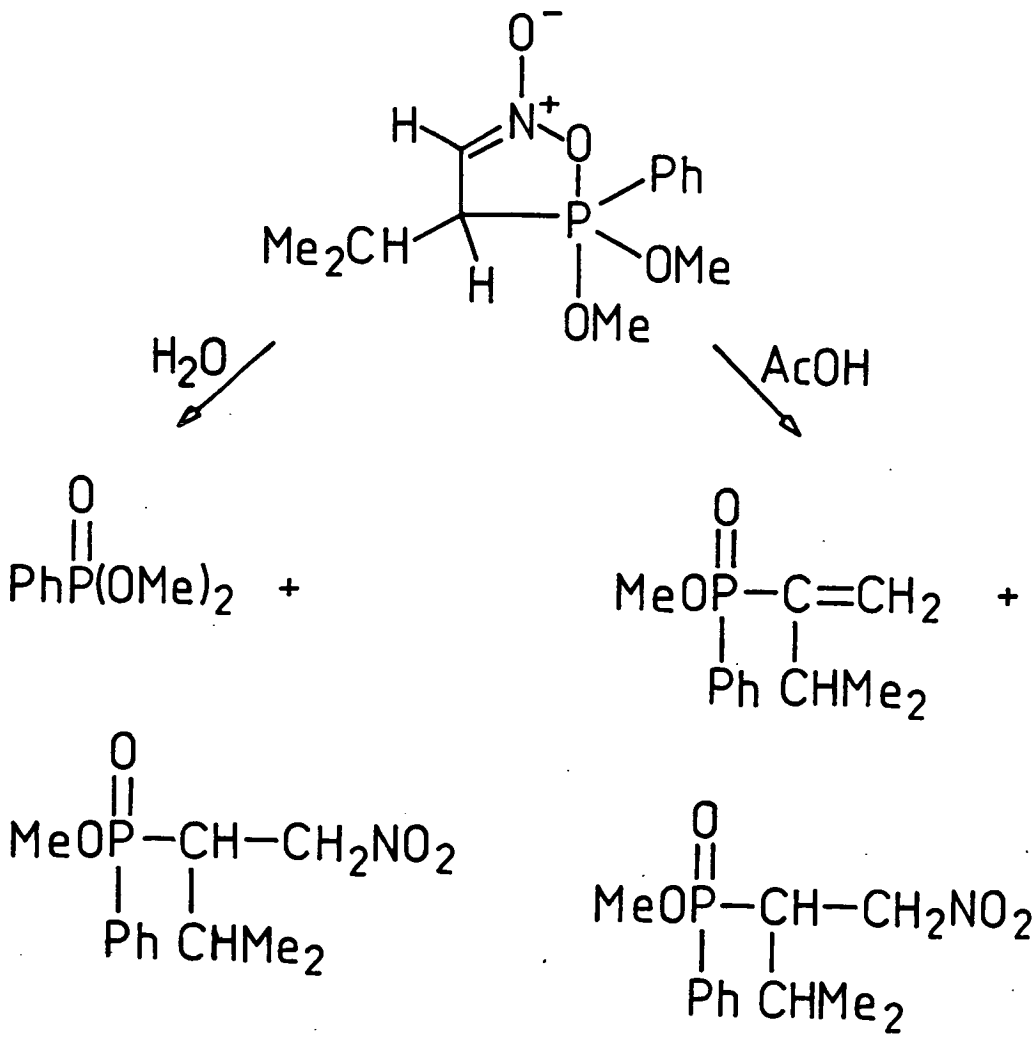
The structure of the product therefore remains in doubt, but even so, this is a remarkable reaction in that the nitro compound is not deoxygenated by the triethyl phosphite, but rearranges instead. A somewhat similar rearrangement has been observed in the formation of 3-hydroxy-1-oxo-3H-indole-2-carboxylic acid by photolysis of o-nitrocinnamic acid,[262] and the related formation of 2-phenylisatogens by photolysis[263] of o-nitrostilbenes or thermolysis[264] of their pyridinium salts in the presence of base.




Scheme 114

D. Hydrolysis of 2-Oxo-1, 2, 5-oxazaphosph(v)oles

Although a number of 2-oxo-1, 2, 5-oxazaphosph(v)oles have been reported in the literature, a systematic study of their hydrolyses has not been undertaken. Gareev[129] has shown that reaction of an oxazaphosphole oxide with both water and acetic acid leads to the formation of a nitrophosphinate (Scheme 115), and an analogous compound has been obtained[265]

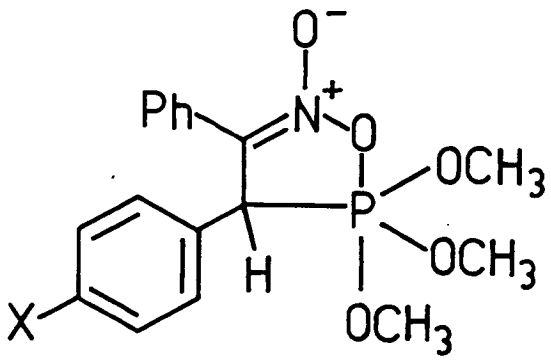



Scheme 115

from the hydrolysis of an oxazaphosphole oxide derived from trimethyl phosphite. In a similar way, protic addition of trialkyl phosphites to β-

nitrostyrenes gives rise to β-nitroethanephosphonates via a postulated phosphorane intermediate.[140]

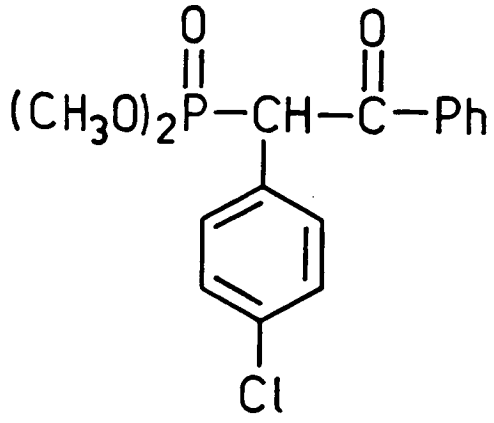
A series of acid catalysed hydrolyses was carried out on phosphoranes (69) in aqueous dioxan with p-toluenesulphonic acid as the catalyst. A preliminary study of the hydrolysis of (69) (X = Cl)



(69)

with 2M hydrochloric acid had shown that products were obtained which had incorporated chlorine from the acid, and for this reason, p-toluenesulphonic acid, with its non-nucleophilic anion, was used.

Hydrolysis of (69) (X = Cl) gave on work-up a white solid identified as the ketone phosphonate (79) (64%) by its spectral data.

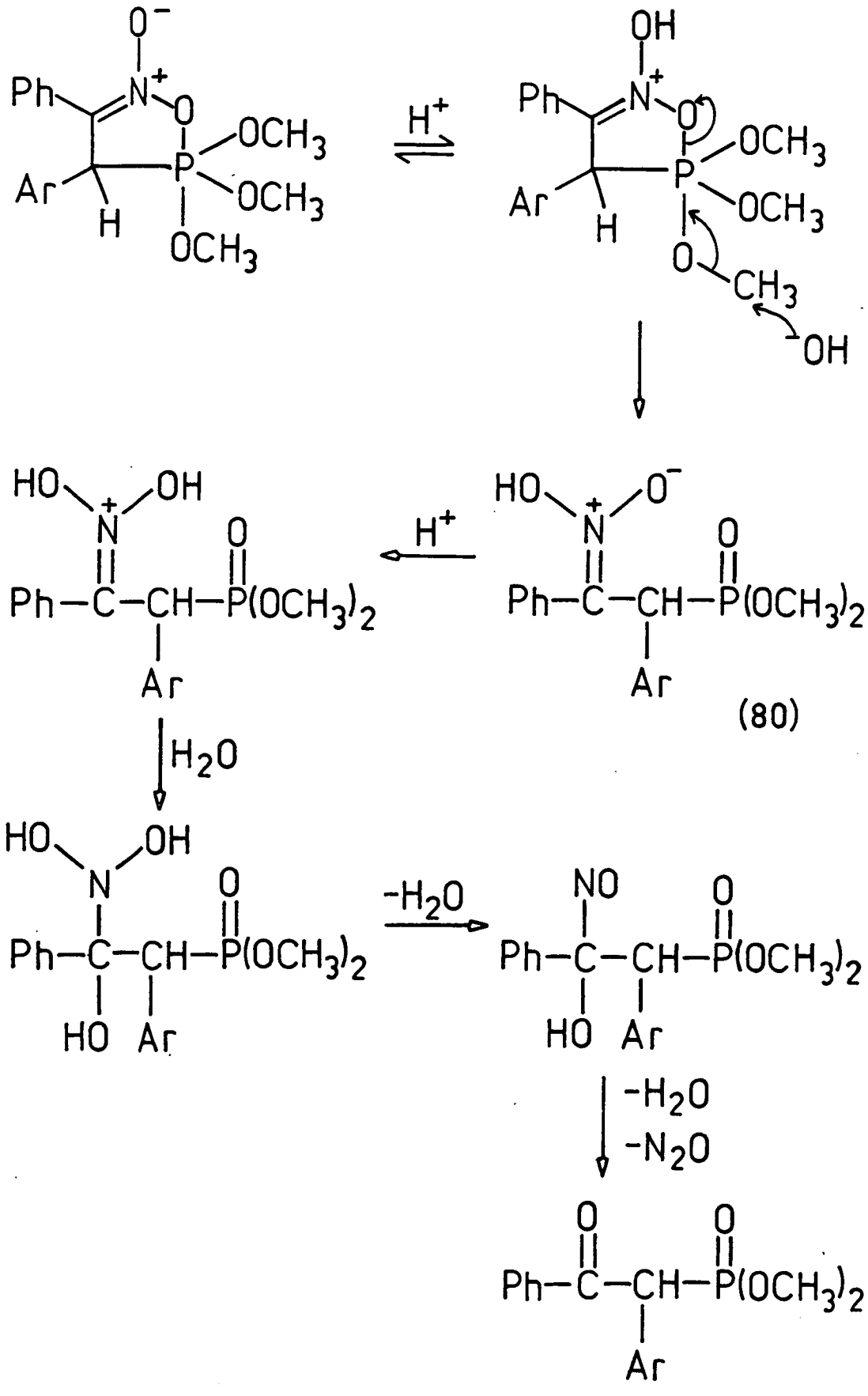


(79)

The I. R. spectrum shows a carbonyl absorption at 1682 $cm^{-1}$ and also characteristic absorptions due to the P=O and POC groupings. The $^{1}H$ n. m. r. clearly shows the dimethyl phosphonate moiety, and also shows

a large one proton doublet due to the isolated proton. A two proton multiplet appears at low field and can be assigned to the o-protons in the phenyl ring, as this is attached to the electron-withdrawing carbonyl group. The mass spectrum exhibits the correct parent ion and has the base peak at m/e 105 due to the benzoyl ion. The only other significant peaks in the mass spectrum were shown by exact mass measurements to be due to a fragment ion of formula $C_{14}H_9Cl$, presumably with the 1-(4-chlorophenyl)-2-phenylethyne structure. This could be considered to arise *via* a cyclic mechanism involving the phosphorus atom and the carbonyl oxygen.

A possible mechanism for the formation of this product is shown in Scheme 116, which is also in accord with the formation of nitrophosphinates and phosphonates described above. The first step is probably a fast equilibrium between the phosphorane and the protonated form, as a $^{31}P$ n.m.r. study of a phosphorane hydrolysis showed only one peak in the P(V) region of the spectrum. Subsequent apical attack[260, 266] by hydroxide ion on the methoxyl group results in ring cleavage and formation of the intermediate (80), which contains a nitro group in the *aci* form. The remainder of the scheme is simply the Nef reaction,[267] which involves acid hydrolysis of primary or secondary aliphatic nitro compounds to aldehydes or ketones respectively. Tautomerism of the *aci* form to the more stable nitro form would lead to the products obtained in the literature studies. The blue and turquoise colours observed in the hydrolysis reactions could be ascribed to the intermediate nitroso compound, as monomeric aliphatic nitroso compounds are generally blue in solution.[268] If this mechanistic scheme is correct,

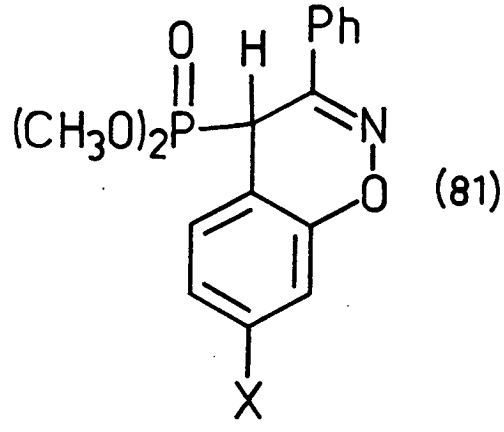


(80)

Scheme 116

then methanol should also be produced in the reaction. The hydrolysis was followed by $^1$H n. m. r. in $d_8$-dioxan using a solution of p-toluenesulphonic acid in deuterium oxide. This showed the appearance of a singlet at 3. 26 δ which was shown by peak enhancement to be due to methanol. The above mechanism therefore seems quite reasonable on the basis of the available evidence.

The hydrolyses of (69) (X = Me) and (69) (X = H) both gave the expected ketone phosphonates in 44% and 40% yield respectively, but there was also another product isolated in ca 10% yield in both cases. This minor product was tentatively identified as the 4H-1,2-benzoxazine phosphonate (81). The spectroscopic evidence leading to this assign-



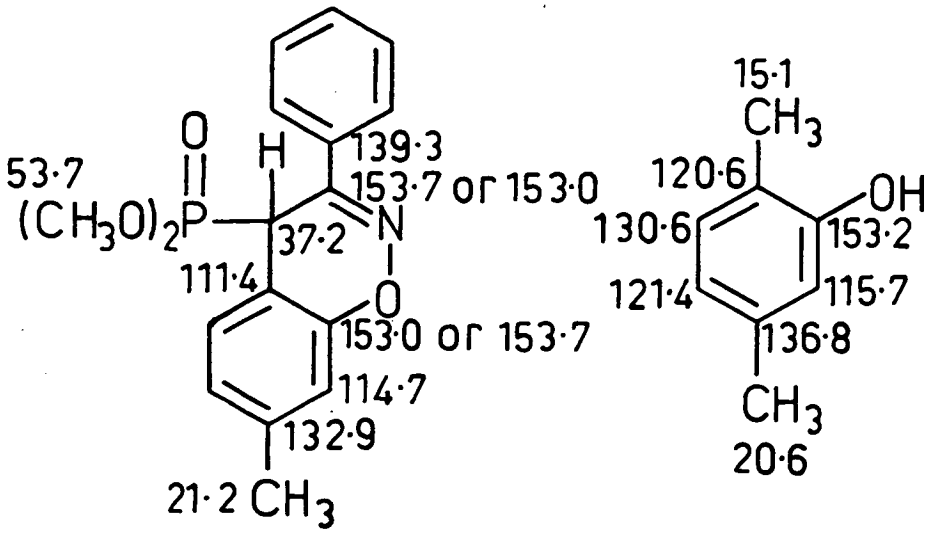

(81)

(a) X = Me

(b) X = H

ment in the case of (81a) is as follows. The I. R. spectrum is not particularly helpful, showing absorptions due to the P=O and POC groupings but little else of any structural value. The $^1$H n. m. r. spectrum shows a number of interesting features. The dimethyl phosphonate moiety is shown quite clearly, and the aryl methyl group shows a seven bond coupling of 2 Hz to the phosphorus. A large one proton doublet is observed due to the CH-P grouping. The aromatic region of the spectrum integrates to only eight protons, showing that an insertion has

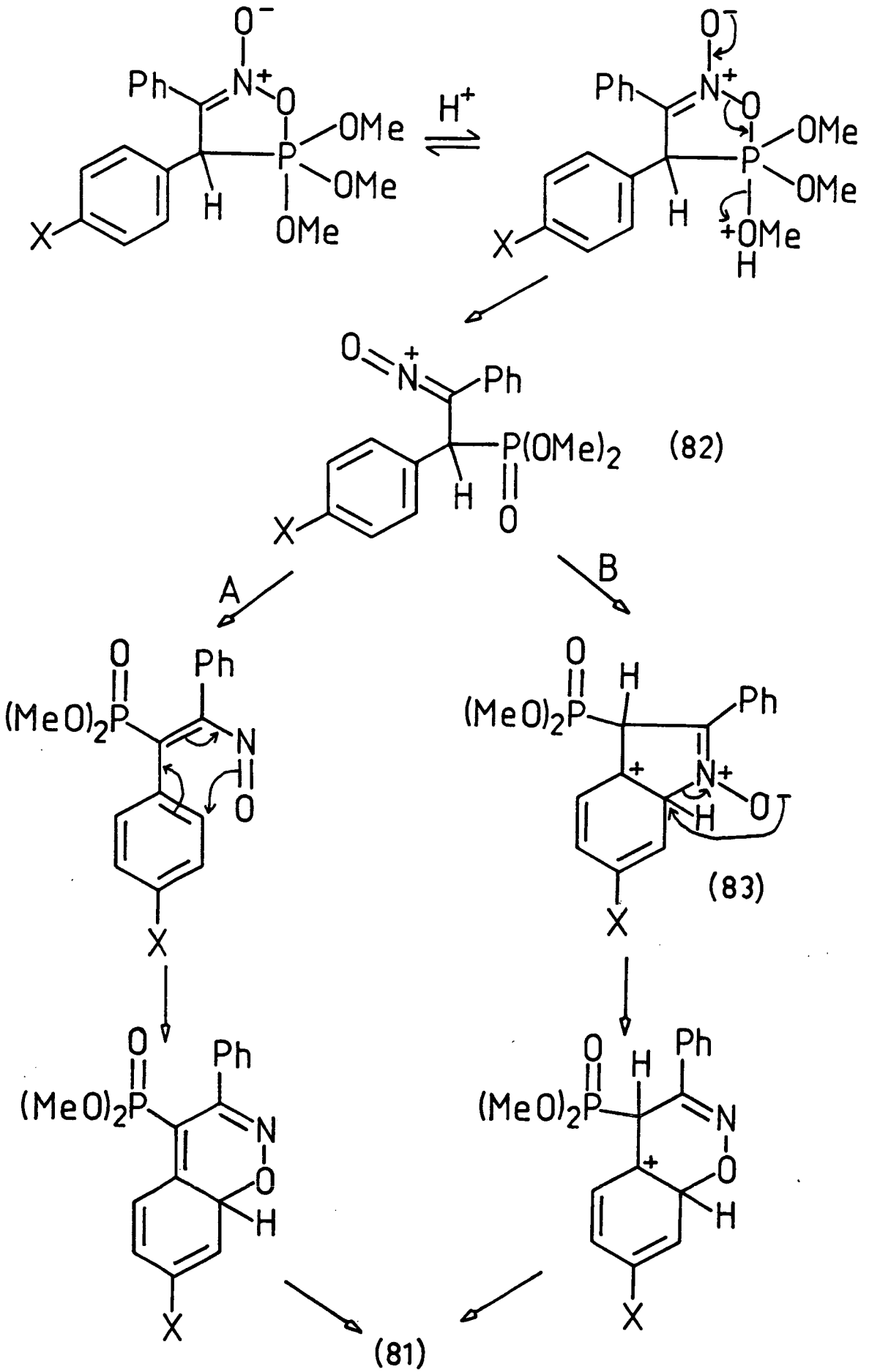
taken place into one of the benzene rings. In addition, it exhibits a very unusual coupling pattern. There is a broad one proton singlet presumably due to the proton between the oxygen and methyl substituents, but far more interesting is the apparent AB pattern, one half of which is phosphorus coupled. This is probably due to the adjacent protons in the aryl ring but the coupling constants are atypically unequal, one being twice the size of the other. This would at first sight appear to indicate that this assignment is incorrect, but the observed peak structure and the proposed structure of the product are not necessarily contradictory. The chemical shifts of the three resonances are so similar that second order effects will be very important and the unequal coupling constants could simply be a consequence of these. In any case, if an insertion occurs into the aryl ring, a 1,2,4-trisubstituted aryl ring must result. The selective phosphorus coupling to only one of the protons is probably no more than a geometric effect. A low field two proton multiplet is also observed in the aromatic region of the spectrum due to the o-protons in the phenyl ring attached to the CNO functionality. The $^{13}C$ n.m.r. also shows that an insertion has taken place. A comparison of the chemical shifts with those observed for 2,5-dimethylphenol is not inconsistent with the postulated structure. Tentative assignments of the observed resonances are shown below. The mass spectrum shows the correct parent ion peak and also exhibits a fragmentation pattern which can be fitted to the above structure. The base peak at m/e 222 arises by loss of $(CH_3O)_2PO$ from the parent ion, and the large peak at m/e 103 is due to PhCN. There is also a peak due to loss of methanol, and an interesting peak at m/e 194 shown by the presence of a metastable




peak to result from fragmentation of the structure at m/e 222. This is probably due to loss of CO giving a fragment with a cyclopentadiene structure. Analogous spectroscopic data was also obtained for (81b).

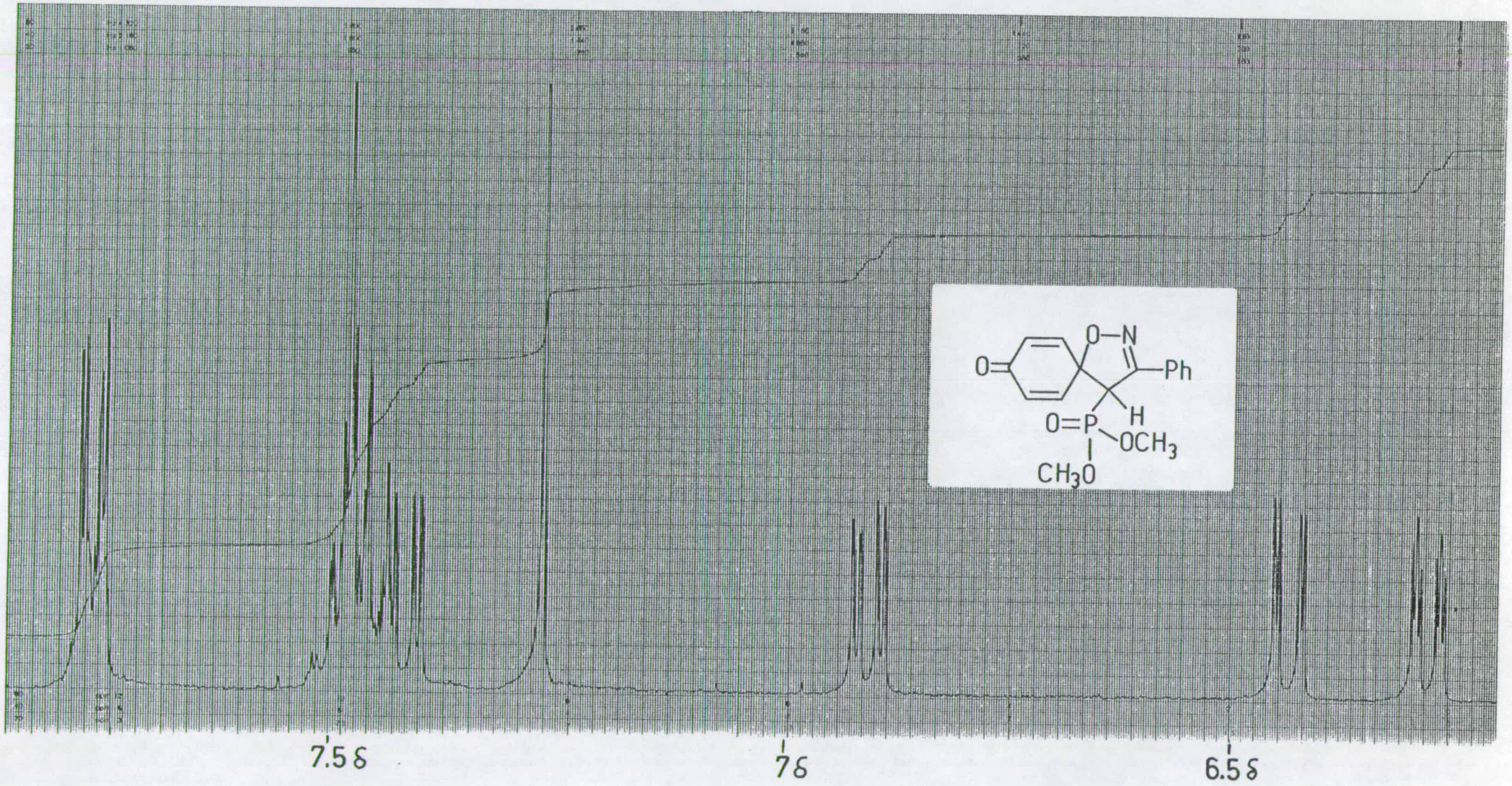
Scheme 117 shows two possible mechanisms for the formation of the benzoxazines. Both involve initial protonation of the apical methoxyl group, a reaction which probably competes with the N-oxide protonation discussed earlier. Subsequent apical loss of methanol and ring opening leads to the intermediate (82) from which two routes to the benzoxazine can be envisaged. Route A involves loss of a proton to give the nitrosoalkene, followed by attack on the ring and [1,3]-hydrogen transfer to give the product. Route B involves electrophilic attack on the ring to give the N-oxide (83) which then rearranges and loses a proton to give the product. Route B seems the less likely because the N-oxide (83) would be expected to lose a proton to give a stable 3H-indole N-oxide, a result which is not observed.

An $^{1}$H n. m. r. study of the hydrolysis of (69) (X = H) showed the disappearance of the phosphorane doublet due to the $sp^{3}$ proton, and



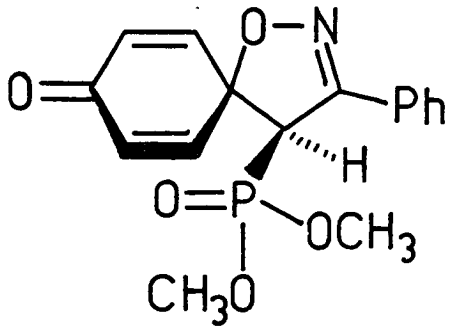
Scheme 117

Fig. 8 Dimethyl 3-phenyl-2-isoxazoline-5-spirocyclohexadien-4'-one-4-phosphonate; $^{1}H$ n. m. r. spectrum-aromatic region.



the simultaneous appearance of the two product doublets and the methanol singlet. When the reaction was almost complete, the integrations of the product doublets and the methanol singlet showed that the two products and the methanol were produced in approximately equimolar amounts, which is consistent with the mechanisms discussed above.

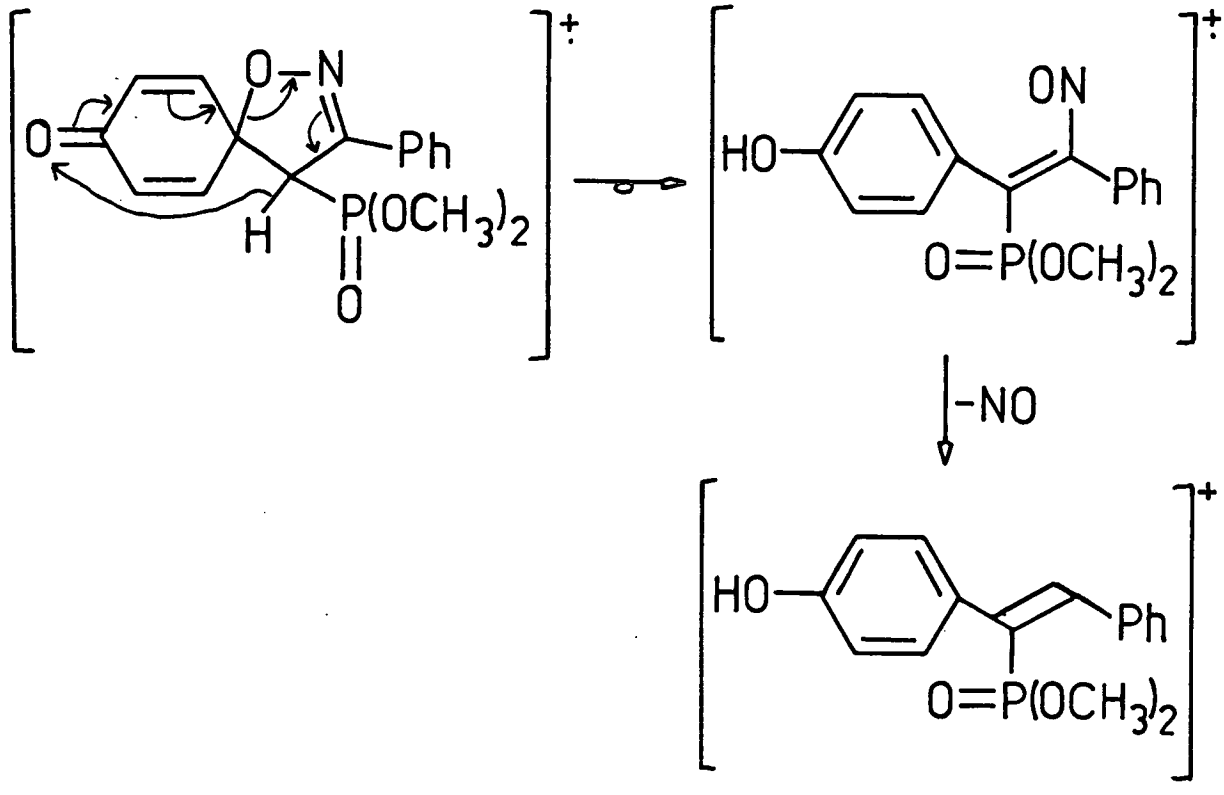
Hydrolysis of (69) (X = OMe) took a quite different course from the others, addition of the acid resulting in rapid formation of a white precipitate identified as the spirodienone (84) (62%). The spectroscopic



(84)

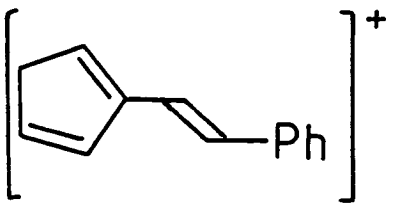
data is entirely consistent with this structure. The I. R. spectrum shows two bands at 1675 and 1636 $cm^{-1}$, characteristic[269] of the cyclohexadienone group. The $^{1}H$ n. m. r. spectrum shows the presence of the dimethyl phosphonate moiety and the proton adjacent to the phosphorus atom. The four protons of the cyclohexadienone ring are non-equivalent and have characteristic chemical shifts.[269,270] Their signals exhibit a variety of long and short range couplings (Fig. 8). There is also a downfield two proton multiplet due to the o-phenyl protons, as the phenyl ring is attached to the electron-withdrawing C=N group. In the $^{13}C$ n. m. r., the carbonyl resonance appears at 184.3 p. p. m. and that due to the C=N group at 155. 0 p. p. m. As expected, the carbon atom attached to the phosphorus exhibits a large one bond coupling (142 Hz), but the $sp^3$ carbon of the cyclohexadienone ring is not coupled to

phosphorus at all. Similar zero two bond carbon-phosphorus coupling constants have been observed in the spectra of certain cyclic phosphines.[271] The mass spectrum is also consistent with structure (84), showing the correct parent ion and fragment ions due to PhCNO (base peak), $(CH_3O)_2PO$, PhCN, and PhO. The peak at m/e 105 is probably due to PhCO, while those at m/e 303 and 165 are assigned on the basis of exact mass measurements. The peak at m/e 303 is a result of loss of NO from the parent ion, a fragmentation not normally observed for isoxazolines. In this case, however, a route leading to a particularly stable fragment ion can be postulated (Scheme 118). The peak at m/e 165



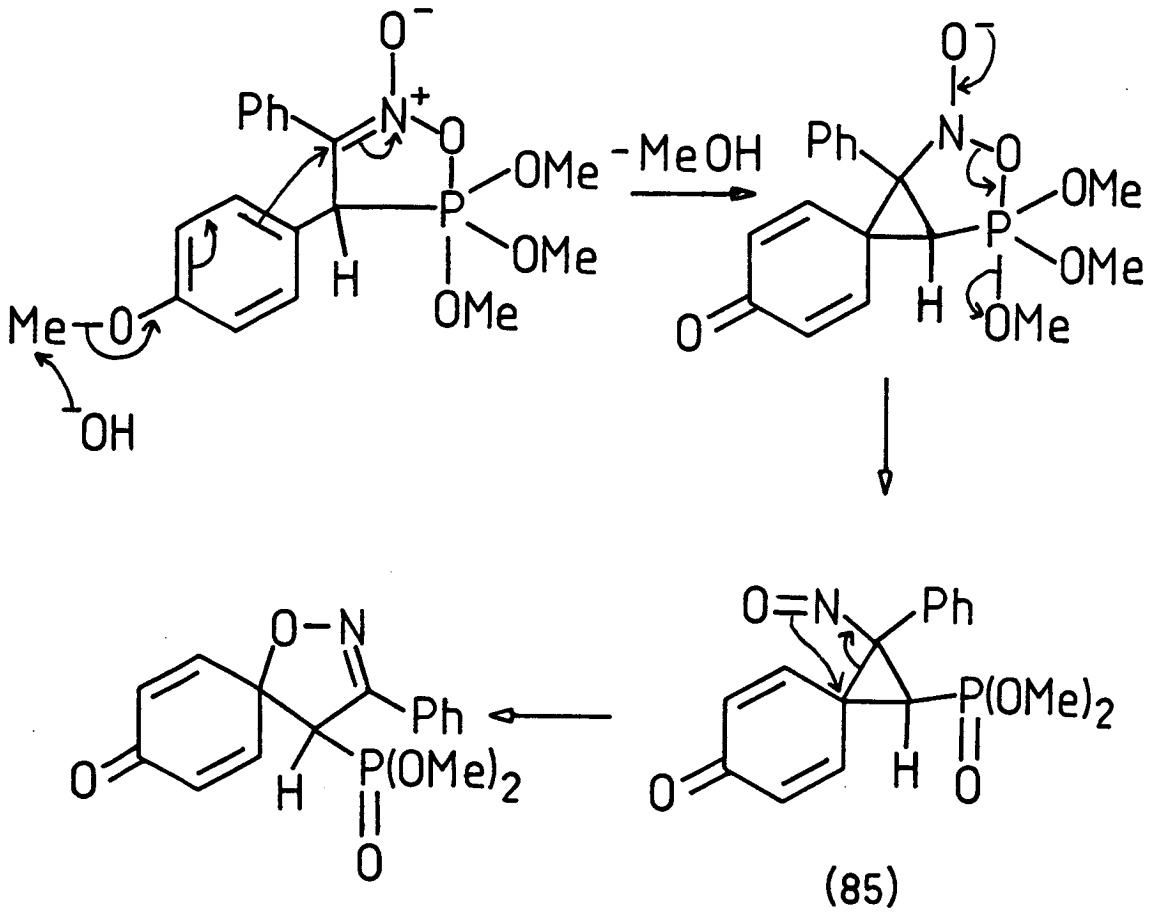

Scheme 118

is most probably due to an ion of formula $C_{13}H_9$ whose structure is almost certainly that shown below. All the available evidence therefore points to the structure of the product being (84).




m/e 165

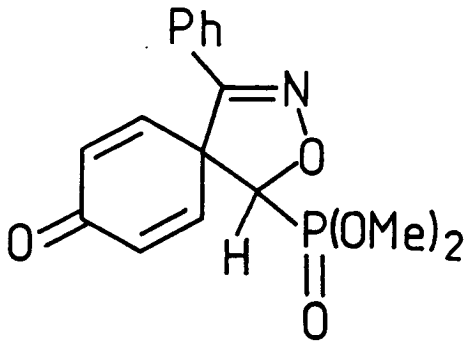
Although the product appears quite complicated, a simple mechanism for its formation can be proposed (Scheme 119). The




Scheme 119

first step involves attack of hydroxide ion on the p-methoxyl group to form the spirodienone system, with loss of methanol. The second step involves ring-opening with apical loss of methoxide ion (or methanol, if the oxygen atom is protonated) to give the nitroso-cyclopropane (85). In accord with the alkene-like reactivity of cyclopropanes, the nitroso

group then attacks[237b] the cyclopropane ring to give the product. It is clear that this is not the only route open to the intermediate (85), however. Attack at the other ring carbon would lead to the alternative product (86), whose structure is also consistent with the I. R. and




(86)

n. m. r. data described above. The crucial evidence against this structure comes from the mass spectrum because a reasonable mechanism for loss of NO cannot be written for this compound. In addition, the peak at m/e 165 cannot be easily explained. In a fairly qualitative way, an $^{1}H$ n. m. r. study of the hydrolysis was consistent with such a mechanism involving formation of two moles of methanol because the volume of methanol required to significantly increase the size of the methanol singlet was much greater than in the other cases investigated, where only one mole of methanol was produced in the reactions. The formation of a spirodienone in an acid catalysed hydrolysis reaction involving a methoxyl group is not without precedent.[272]

In conclusion, one can state that in the absence of complicating substituent participation, the principal hydrolysis reaction of the oxazaphosphole oxides involves initial N-oxide protonation followed by ring-opening to give products derived from the aci-nitro compound. In competition with this is apical methoxyl protonation leading to minor products such as the benzoxazines.

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